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16. ABSTRACT
This report describes studies of the hydrocarbons, biocides, sulfur, and related substances discharged from structures in the Buccaneer Gas and Oil Field, their distribution and fates in the surrounding environment, and the assessment of their ecological effects. More than 120 substances have been identified in produced water discharges from the production platforms, however the major pool of contaminants in the region of the Buccaneer Field is in the surficial sediments. They contain concentrations as high as 50 ppm of 'fresh' petroleum alkanes, and concentration gradients are clearly seen. Petroleum alkanes were usually detected at the air/sea interface in the mixing zone below the discharge pipes, but were found only occasionally in other seawater samples. Some seawater samples contained bacterial hydrocarbons which may have been produced by sulfur-bacteria supported by the discharged sulfur - a possible indirect source of alkanes attributable to oil and gas production activities. A degree of correlation was found between the feeding habits of some fish and their content of petroleum hydrocarbons. There was no evidence for biomagnification of hydrocarbons in the web. Biogenic hydrocarbons usually predominated over petroleum hydrocarbons in biota samples. Elemental sulfur, a major component of the effluents is a nutrient for sulfur-bacteria and may contribute to the food web. (Author modified)

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VOL. V - HYDROCARBONS, BIOCIDES AND SULFUR

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A report to the Environmental Protection Agency on work conducted under provisions of Interagency Agreement EPA-IAG-D5-E693-EO during 1975-1980.

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Volume V - HYDROCARBONS

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LIST OF VOLUMES

This Milestone Report is printed in six separate volumes:

Volume I - SEDIMENTS, PARTICULATES AND VOLATILE HYDROCARBONS

Work Unit 2.3.2 — Investigations of Surficial Sediments, Suspended Particulates and Volatile Hydrocarbons at Buccaneer Gas and Oil Field

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Volume II - FISHES AND MACRO-CRUSTACEANS

Work Unit 2.3.5/2.3.8 — Pelagic, Reef and Demersal Fishes, and Macro-crustaceans/Biofouling Communities

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Volume III - BACTERIA

Work Unit 2.3.7 — Bacteriology of a Gulf of Mexico Gas and Oil Field

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Volume IV - CURRENTS AND HYDROGRAPHY

Work Unit 2.3.9 Currents Patterns and Hydrography of the Buccaneer Field and Adjacent Waters

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Volume V - HYDROCARBONS

Work Unit 2.4.1 Hydrocarbons, Biocides and Sulfur

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Volume VI - TRACE METALS

Work Unit 2.4.2 Trace Metals

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FOREWORD

Increased petroleum development of the outer continental shelf (OCS) of the United States is anticipated as the U.S. attempts to reduce its dependency on foreign petroleum supplies. To obtain information concerning the environmental consequences of such development, the Federal Government has supported major research efforts on the OCS to document environmental conditions before, during, and after oil and gas exploration, production, and transmission. Among these efforts is the *Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico*, a project funded by the Environmental Protection Agency (EPA) through interagency agreement with the National Oceanic and Atomospheric Administration (NOAA) and managed by the National Marine Fisheries Service (NMFS), Southeast Fisheries Center (SEFC), Galveston Laboratory, in Galveston, Texas. Initiated in the autumn of 1975, the study was completed in 1980. Its major products have been annual reports disseminated by the National Technical Information Service, data files archived and disseminated by NOAA's Environmental Data and Information Service, and research papers written by participating investigators and published in scientific or technical journals. Results have also been made available through EPA/NOAA/NMFS project reviews and workshops attended by project participants, and various governmental (Federal and State), private, and public user groups. The final product are these milestone reports summarizing the findings of the major investigative components of the study.

Objectives of the project were (1) to identify and document the types and extent of biological, chemical and physical alterations of the marine ecosystem associated with Buccaneer Gas and Oil Field, (2) to determine specific pollutants, their quantity and effects, and (3) to develop the capability to describe and predict fate and effects of Buccaneer Gas and Oil Field contaminants. The project used historical and new data and included investigations both in the field and in the laboratory. A brief Pilot Study was conducted in the autumn and winter of 1975-76, followed by an extensive biological/chemical/physical survey in 1976-77 comparing the Buccaneer Gas and Oil Field area with adjacent undeveloped or control areas. In 1977-78, investigations were intensified within Buccaneer Gas and Oil Field, comparing conditions around production platforms, which release various effluents including produced brine, with those around satellite structures (well jackets) which release no effluents. In 1978-79, studies around Buccaneer Gas and Oil Field structures focused on (1) concentrations and effects of pollutants in major components of the marine ecosystem, including seawater, surficial sediments, suspended particulate matter, fouling community, bacterial community, and fishes and macro-crustaceans, (2) effects of circulation dynamics and hydrography on distribution of pollutants, and (3) mathematical modeling to describe and predict sources, fate and effects of pollutants. The final year, 1979-80, of study continued to focus on items (1) and (2) and on preparation of the milestone reports which represented the final products of this study.

This project has provided a unique opportunity for a multi-year investigation of effects of chronic, low-level contamination of a marine ecosystem associated with gas and oil production in a long-established field. In many respects, it represents a pioneering effort. It has been made possible through the cooperation of government agencies, Shell Oil Company (which owns and operates the field) and various contractors including universities and private companies. It is anticipated that the results of this project will impact in a significant way on future decisions regarding operations of gas and oil fields on the OCS.

Charles W. Caillouet, Project Manager
Chief, Environmental Research Division
and
William B. Jackson and E. Peter Wilkens,
Editors

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LIST OF ARCHIVED DATA

Data available from U.S. Department of Commerce, NOAA, EDIS,
National Oceanographic Data Center, Washington, D.C. 20235

Year	Data Type	NODC Accession Number
1976-1977	Demersal Fish	78-0501
1976-1977	Sediment	78-0501
1976-1977	Birds	78-0501
1976-1977	Ichthyoplankton	78-0501
1976-1977	Pelagic Fish	78-0501
1976-1977	Plankton	78-0501
1976-1977	Sessile Fauna	78-0501
1976-1977	Total Organics	78-0501
1976-1977	Hydrocarbons	78-0501
1976-1977	Fish Determination	78-0501
1976-1977	Ocean Serial Stations	78-0501
1976-1977	Trace Metals	78-0501
1976-1977	Benthos	78-0501
1976-1977	Drift Bottle Releases	78-0501

Year	Data Type	NODC Accession Number
1977-1978	Brine Dye Release	80-0423
1977-1978	Fish Bioassay	80-0423
1977-1978	Ichthyoplankton	80-0423
1977-1978	Food Habits-Station	80-0423
1977-1978	Food Habits-Stomach	80-0423
1977-1978	Reef Fish Census	80-0423
1977-1978	Pelagic Fish Census	80-0423
1977-1978	Biofouling	80-0423
1977-1978	Transponding Buoy (2 Files)	80-0423
1977-1978	Drift Bottle Release/Recovery	80-0423
1977-1978	Dye Study-station	80-0423
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Year	Data Type	NODC Accession Number
1977-1978	Respirometry Experiment	80-0423
1977-1978	Trace Metals - Sediment (Diver Core)	80-0423
1977-1978	Sediment Size Analysis	80-0423
1977-1978	Stomach Contents	80-0423
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1977-1978	Shrimp Bioassay	80-0423
1977-1978	Trace Metals	80-0423
1977-1978	Trapped Suspended Sediment	80-0423
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1977-1978	Stomach Contents	80-0461
1977-1978	Demersal Fish	80-0461
1977-1978	Shrimp Bioassay	80-0461
1977-1978	Trace Metals	80-0461
1977-1978	Trapped Suspended Sediment	80-0461

Year	Data Type	NODC Accession Number
1978-1979	Stomach Contents	80-0416
1978-1979	Clay Mineralogy	80-0416
1978-1979	Bioassay (Toxicity)	80-0416
1978-1979	Algae	80-0416
1978-1979	Tagging	80-0416
1978-1979	Histopathology and Bacteriology	80-0416
1978-1979	Morphometric	80-0416
1978-1979	Benny Census	80-0416
1978-1979	Biomass Samples - Weight and Barnacles	80-0416
1978-1979	Pistol Shrimp and Stone Crab	80-0416
1978-1979	Biomass - Large Cryptic Samples	80-0416
1978-1979	Surficial Sediments	80-0416
1978-1979	Suspended Particulates	80-0416
1978-1979	Sediments	80-0416

Year	Data Type	NODC Accession Number
1978-1979	Pb - 210	80-0416
1978-1979	Bacteria - Enumeration	80-0416
1978-1979	Bacteria - Degradation Rates	80-0416
1978-1979	Bacteria - Taxonomy	80-0416
1978-1979	Bacteria - Growth Characteristics	80-0416
1978-1979	Trace Metals	80-0416
1978-1979	Trace Metals - Organism, Sediment, Water	80-0416
1978-1979	Hydrography	80-0416
1978-1979	Electromagnetic Current Meter	80-0416
1978-1979	Total Suspended Solids	80-0416
1978-1979	Continuous Current Meter	80-0416
1978-1979	Meteorological Data	80-0416
1978-1979	Wave Data	80-0416
1978-1979	Hydrocabons, Biocides and Sulfur	80-0416
1978-1979	Respirometry	80-0416

Year	Data Type	NODC Accession Number
1979-1980	Data being archived, will be available in late 1980	TBA

INTRODUCTION

Location of Study Area

The area selected for study is the operational Buccaneer Gas and Oil Field located approximately 49.6 kilometers (26.8 nautical miles) south southeast of the Galveston Sea Buoy off Galveston, Texas (Figure 1). This field was selected in 1975 as the study area because: (a) the field had been in production for about 15 years, which time had allowed full development of the associated marine communities; (b) it was isolated from other fields which facilitated the selection of an unaltered area (for comparison) within a reasonable distance of the field; (c) it produced both gas and oil that represented sources of pollutants from marine petroleum extraction; (d) its location simplified logistics and reduced the cost of the research; and (e) the Texas offshore area had not been fully developed for gas and oil production but was expected to experience accelerated exploitation in the future.

Operation History of Buccaneer Field

Buccaneer Field was developed by Shell Oil Company in four offshore blocks leased in 1960 and 1968 as follows:

Year	Lease Number	Block Number	Acreage	Hectares
1960	G0709	288	2,790	1,129
1960	G0713	295	4,770	1,930
1960	G0714	296	4,501	1,821
1968	G1783	289	2,610	1,056

In development of the field, 17 structures were built; two are production platforms, two are quarters platforms, and 13 are satellite structures surrounding well jackets. Initial exploratory drilling began about mid-summer of 1960 with mobile drilling rigs. When (as the result of the exploratory drilling) proper locations for platforms were selected, the permanent production platforms were constructed.

There have been no reports of major oil spills from this field. There have been some reported losses of oil due to occasional mechanical failure of various pieces of equipment. The largest reported spill was three barrels in 1973. The reported oil spill chronology and quantity for Buccaneer Field is as follows:

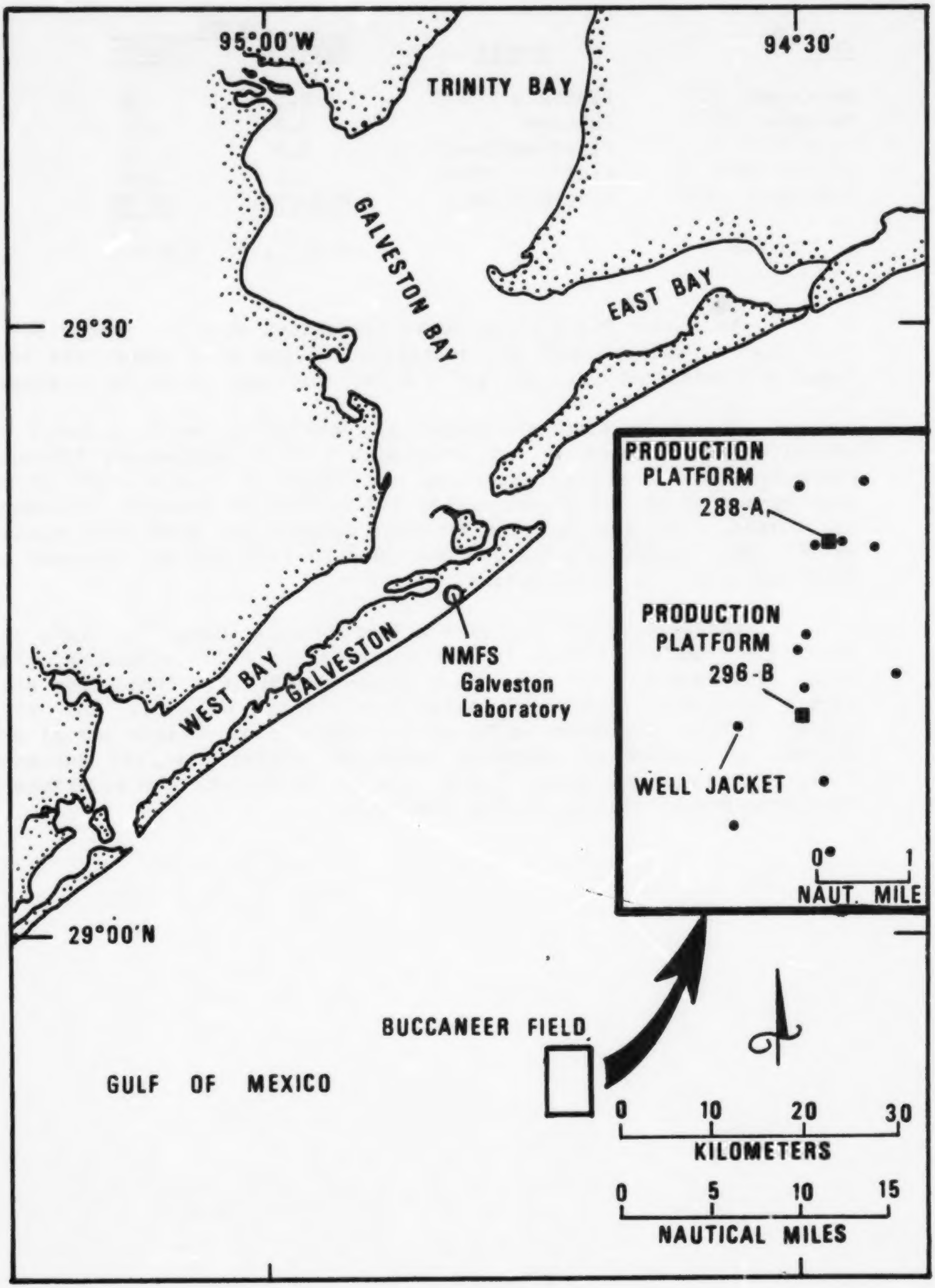
95°00'W
94°30'
TRINITY BAY
GALVESTON BAY
EAST BAY
29°30'
WEST BAY
GALVESTON
NMFS
Galveston
Laboratory
29°00'N
PRODUCTION
PLATFORM
288-A
PRODUCTION
PLATFORM
296-B
WELL JACKET
0
1
NAUT. MILE
BUCCANEER FIELD
GULF OF MEXICO
0
10
20
30
KILOMETERS
0
5
10
15
NAUTICAL MILES

FIGURE 1. LOCATION OF BUCCANEER FIELD

Date	Source	Amount Barrels	Liters
September 1973	Platform 296-B	0.5	79
November 1973	Unknown	3.0	477
July 1974	Platform 296-B	0.5	79
August 1974	Platform 296-B	1.7	265
September 1975	Platform 288-A	0.2-0.4	38-56
Totals		5.9-6.1	938-956

Buccaneer Field first began operations with the production of oil. Later, when significant quantities of gas were found, the field began producing both oil and gas and has continued to do so to date.

The production platforms and satellites (well jackets) are connected by a number of pipelines with a 50.8 centimeters (20-inch) diameter main pipeline connecting the field to shore. All of the pipelines that are 25.4 centimeters (10 inches) or greater in diameter are buried. The Blue Dolphin Pipeline Company was granted a pipeline permit (No. G1381, Blocks 288 and 296) in 1965 and has operated the pipeline since its construction.

Buccaneer Field occupies a limited area (about 59.3 km^2; 22.9 sq. statute miles) leased in the northwestern Gulf of Mexico. Four types of structures are located in Buccaneer Field: production platforms, quarters platforms, satellites (well jackets), and flare stacks. These are shown in Figure 2, which is an oblique aerial photograph of production platform 288-A and vicinity within Buccaneer Field. A map of Buccaneer Field, (Figure 3) depicts the locations of platforms and satellites within the field.

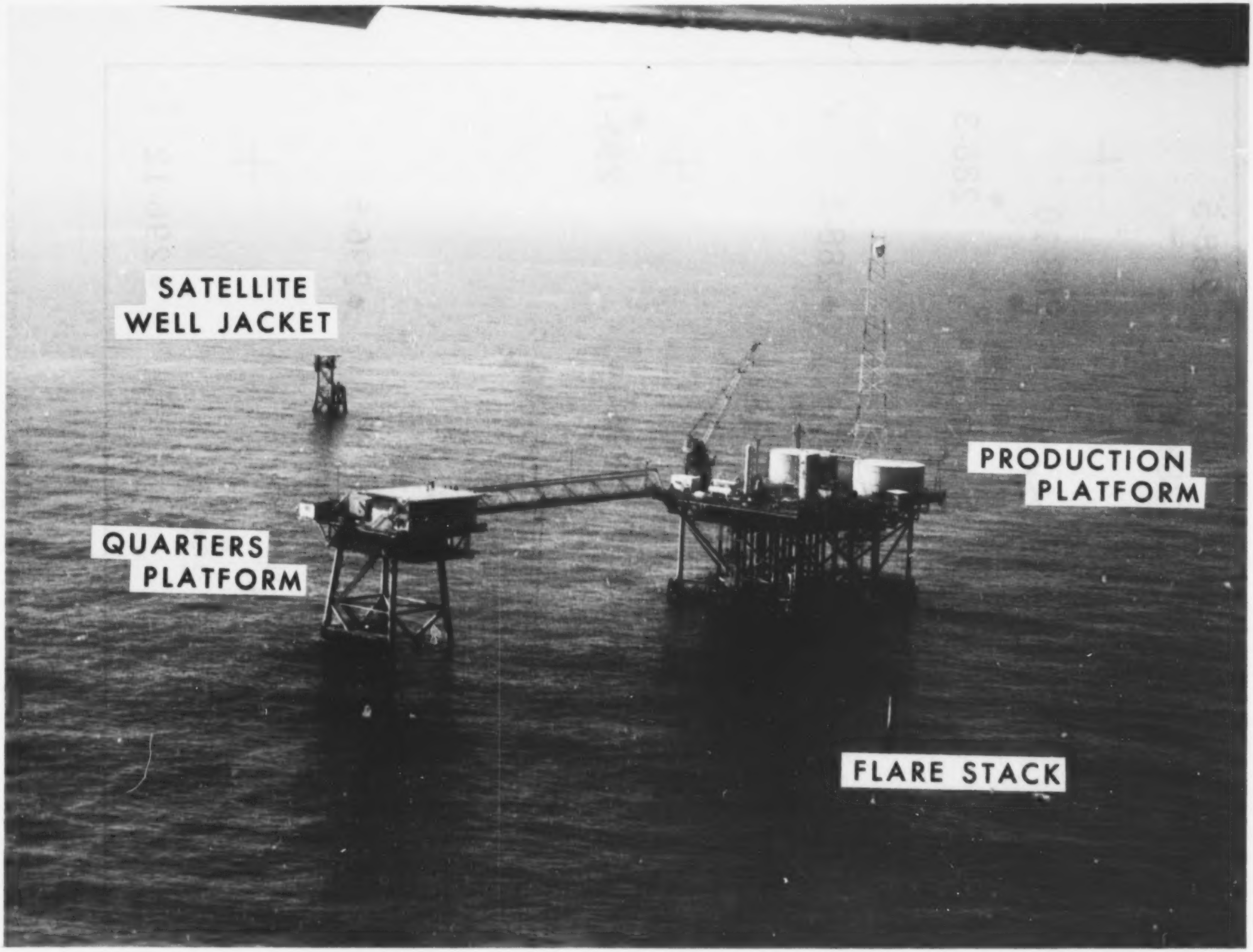
SATELLITE WELL JACKET
QUARTERS PLATFORM
PRODUCTION PLATFORM
FLARE STACK

FIGURE 2. BUCCANEER FIELD STRUCTURES

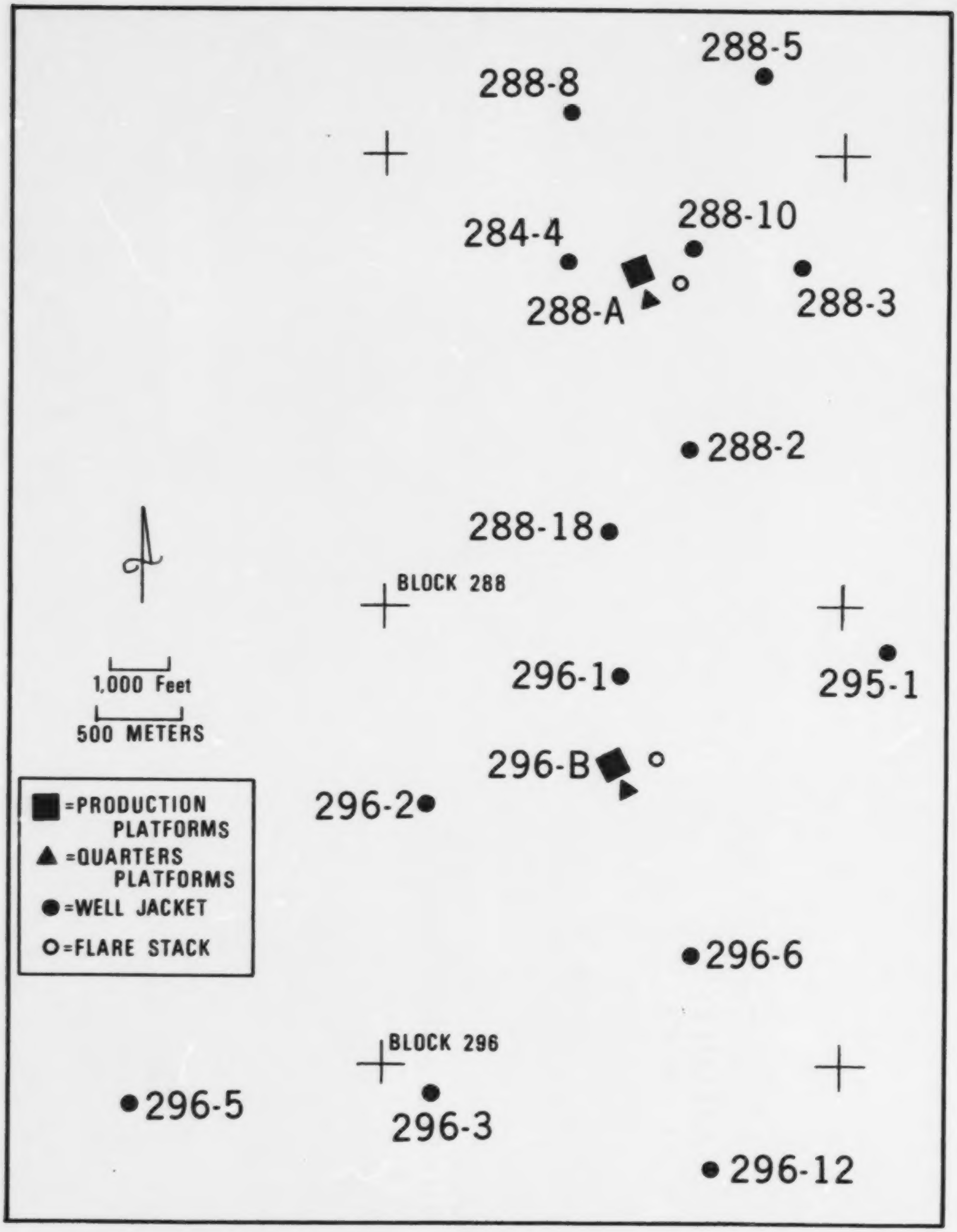
288-5
288-8
288-10
284-4
288-A
288-3
288-2
288-18
BLOCK 288
296-1
295-1
1,000 Feet
500 METERS
296-B
296-2
■ =PRODUCTION PLATFORMS
▲ =QUARTERS PLATFORMS
● =WELL JACKET
○ =FLARE STACK
296-6
BLOCK 296
296-5
296-3
296-12

FIGURE 3. SHELL OIL COMPANY'S ALPHANUMERICAL IDENTIFICATION OF BUCCANEER GAS AND OIL FIELD STRUCTURES

WORK UNIT 2.4.1 - HYDROCARBONS, BIOCIDES AND SULFUR

University of Houston

B. S. Middleditch, Ph.D.

PREFACE

A detailed study of the Buccaneer Gas and Oil Field was preceded by a pilot study conducted by scientists from Texas A&M University. One of the conclusions of the pilot study was that there was sufficient evidence for petroleum hydrocarbons in the environment in the vicinity of the Buccaneer Field to warrant inclusion of a hydrocarbon study in the main project (Giam, 1976). Contracts awarded to the University of Houston enabled it to perform the hydrocarbon study during all four years of the project (1976-1980).

Our study plan was modified many times as we learned more about the hydrocarbon ecology of the Buccaneer Field, and some additional tasks were added as the need arose. Very early on in the study we found moderate concentrations of squalene in the produced water discharges from the production platforms. This was indicative of the presence of bacteria in the effluents. Discussions with the platform operators revealed their use of biocides to suppress the populations of sulfur-bacteria, which produce corrosive metabolites. We also noted that the effluents contained comparatively high concentrations of elemental sulfur. We accordingly included analyses of the biocides and sulfur in our protocol. We also performed a limited number of analyses of selected lipids in some samples and occasionally encountered such substances as antioxidant food additives in some samples. All of these findings are described here in appropriate detail, although the title of the report reflects only the title of the contract in the later years of the study.

ABSTRACT

This report describes studies of the hydrocarbons, biocides, sulfur, and related substances discharged from structures in the Buccaneer Gas and Oil Field, their distribution and fates in the surrounding environment, and an assessment of their ecological effects.

More than 120 substances have been identified in produced water discharges from the production platforms. These substances include n-alkanes, branched alkanes, cycloalkanes, olefins, aromatic hydrocarbons, alkylated aromatic hydrocarbons, biocides, and sulfur. Concentrations as high as 12 ppm of C_{12} to C_{38} alkanes, 170 ppb of methylnaphthalenes, 5 ppb of benzo[a]pyrene, and 1200 ppm of elemental sulfur were measured. Organic toxic pollutants (priority pollutants) detected in concentrations higher than 10 ppb were acenaphthylene, benzene, ethylbenzene, naphthalene, and toluene. Acrolein was employed as a biocide during the latter part of the study, but it was not detected in effluent samples. The discharge rate of produced water varies over a wide range, but it averaged about 1000 bbl (1.6×10^5 liters) per day toward the end of the study. Based on the mean concentrations of constituents throughout the study, the annual discharge of alkanes and elemental sulfur was, respectively, 73 kg and 27 metric tons.

The major pool of contaminants in the region of the Buccaneer Field is in the surficial sediments. They contain concentrations as high as 50 ppm of "fresh" petroleum alkanes, and concentration gradients are clearly seen. While the concentration of elemental sulfur in the effluents is considerably higher than that of the alkanes, sulfur concentrations in the surficial sediments are comparable to those of the alkanes. This observation indicates that sulfur is dispersed and/or degraded in a manner different from that which is applicable to the alkanes.

Petroleum alkanes were usually detected at the air/sea interface in the mixing zone below the discharge pipes, but were found only occasionally in other seawater samples. Some seawater samples contained bacterial hydrocarbons which may have been produced by sulfur-bacteria supported by the discharged sulfur - a possible indirect source of alkanes attributable to oil and gas production activities.

Many different animal species were examined during this study. Petroleum hydrocarbons were encountered in some barnacles, fish, shrimp, and other organisms. A degree of correlation was found between the feeding habits of some fish and their content of petroleum hydrocarbons. Generally, those which fed on components of the platform fouling community contained higher concentrations of petroleum hydrocarbons than those which fed in the water column. Moreover, hydrocarbon concentrations were usually higher in the livers of these fish than in other tissues.

There was no evidence for biomagnification of hydrocarbons in the food web. Biogenic hydrocarbons usually predominated over petroleum hydrocarbons in biota samples.

Acrolein was never detected in effluent samples, even though it was added to the produced water to suppress the populations of sulfur-bacteria. A scavenger is added by the platform operators to the effluent stream to remove excess acrolein prior to discharge.

Elemental sulfur is the major component of the effluents, but it is of low toxicity and is dispersed and/or degraded more efficiently than the petroleum hydrocarbons. This substance is a nutrient for sulfur-bacteria and may contribute to the food web.

This report was submitted in partial fulfillment of Contract No. NA79-GA-C-00039 by the University of Houston, under the sponsorship of the Environmental Protection Agency, as a component of a comprehensive study of the Buccaneer Gas and Oil Field managed by The National Marine Fisheries Service SEFC Galveston Laboratory under the provisions of Interagency Agreement EPA-IAG-D5-E693-EO. This report covers the period April 1, 1976 to August 31, 1980, and work was completed as of August 31, 1980.

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ACKNOWLEDGMENTS

With the exception of some of the samples collected from the platforms, almost all of the samples which we analysed were collected by other participants in this study. For this assistance, we are particularly indebted to Benny Gallaway, John Anderson, Nick Fotheringham, James Brooks, John Finucane, Ian Workman, and their colleagues (too numerous to mention here).

Laboratory examinations of the samples were conducted with the assistance of Brenda Basile, Evelyn Chang, David West, Mark Spain, Stephen Missler, Rickey Cheung, Alexander Magro, and a number of undergraduate students who passed through our laboratory during the past four years.

Many of the conclusions synthesized from our data were formulated during formal and informal discussions with other participants in this study. It is difficult to recall the sources of individual suggestions, but information on the nature of the Buccaneer food web from Benny Gallaway and his colleagues is worthy of special acknowledgment.

This study could not have been performed without the cooperation of Shell Oil Company. The company allowed us access to their platforms, arranged helicopter transportation on many occasions, and also provided answers to our questions concerning activities in the Field.

SECTION 1

INTRODUCTION

There is a considerable body of information available concerning the effects of large quantities of spilled oil (from tanker wrecks, pipeline breaks, drilling blowouts, etc.) on the marine environment. Less is known about the environmental effects of chronic low-level exposure to oil. There have been a few investigations performed in the region of natural seeps and of oil refineries which have given some indication of the resilience of ecosystems to such perturbations. Most studies of the environmental effects of offshore hydrocarbon production have related to the overall ecological well-being of the region in question, rather than focussing on specific, measurable effects to quantify their significance. In view of the increasing density of offshore production activities in the Gulf of Mexico, and their impending inauguration and/or expansion at other locations around the coastline of the United States, the Buccaneer Gas and Oil Field Study was inaugurated with the following specific objectives:

(1) to identify and document the types and extent of biological, chemical, and physical alterations of the marine ecosystem associated with the Buccaneer Gas and Oil Field;

(2) to determine specific pollutants, their quantity, and effects; and

(3) to develop the capability to describe and predict fate and effects of Buccaneer Gas and Oil Field Contaminants.

The project was divided into a number of different work units: some were performed by the National Marine Fisheries Service, while others were carried out under contract. A pilot study performed by scientists from Texas A&M University indicated that there was sufficient evidence for petroleum hydrocarbons in the environment in the vicinity of the Buccaneer Field to warrant inclusion of a hydrocarbon study in the main project (Giam, 1976). Contracts awarded to the University of Houston enabled it to perform the hydrocarbon study during all four years of the project (1976-1980). During the course of this work, the scope of the hydrocarbon study was extended to include consideration of biocides employed on the production platforms, elemental sulfur, and other related substances. The specific objectives of the hydrocarbon study were:

(1) investigation of the composition of the discharges from structures in the Buccaneer Field; → V-2

wt / fenP-1

(2) study of the distribution of components of the discharges in the surrounding environment; and

(3) assessment of the ecological significance of these findings, particularly in relation to the overall objectives of the Buccaneer Gas and Oil Field Study.

This report describes the hydrocarbon study. Other components of the Buccaneer Gas and Oil Field Study are dealt with in companion reports. Previously published interim reports, papers published in the scientific literature, and presentations at symposia for all components of the Buccaneer Gas and Oil Field Study are listed in a bibliography in the editorial section preceding this report.

SECTION 2

RECOMMENDATIONS

The conventional method of assessing effluents from offshore production platforms has included measurements of "total oil" by spectrophotometric methods. Our early results showed that it was more appropriate to consider the effluents as a medium containing a number of individual substances; different relative concentrations of these substances could be present in effluent samples containing the same amount of "total oil." During earlier reviews of our research, we suggested that monitoring of individual toxic components of the effluents would be more appropriate than monitoring "total oil." The proposed new Ocean Discharge Criteria (Federal Register, February 12, 1980) include a provision for monitoring effluents for a specific list of toxic pollutants ("priority pollutants").

The intent of these proposed regulations is to protect the environment from exposure to harmful amounts of specific substances with known toxic properties. It appears that the main concern in drafting these regulations was related to limiting the concentrations of toxic substances in the mixing zone below the discharge pipe. The assumption appears to have been made that there is no other location in the region of an oil field which contains significant quantities of contaminants.

We have indeed found that the mixing zone is the only component of the water column in which measurable quantities of petroleum hydrocarbons and sulfur can be seen. Dispersion of these contaminants appears to be rapid and efficient. Observations by Gallaway (1980) indicate that there is only minimal damage to the platform fouling community which can be ascribed to the discharge. If the rate of discharge of produced water from the platforms were to be increased, we are tempted to suggest that little, if any, additional damage to the fouling community would result. If, however, the concentration of the contaminants in the discharge were to be increased beyond a critical level, the factors which control dispersion and dilution in the water column may be insufficient to protect the fouling community from significant damage. Under such circumstances, effects might also be transmitted to other components of the food web. We have insuffecent information to determine the critical concentration of contaminants at this time, so we are unable to recommend any specific increase in permitted concentrations of contaminants. This appears to be the philosophy of the proposed Ocean Discharge Criteria: limits are imposed upon the concentrations of components of the discharges based upon the state-of-the-art of analytical chemistry, rather than on an assessment of potential harm to the environment.

We feel that some consideration should be given also to the pool of contaminants discovered in the surficial sediments below the production platforms. We venture to suggest that the sediment concentrations of these contaminants depend upon the total quantities of contaminants discharged from the production platforms rather than the concentrations of contaminants in the discharges. Of course, other factors such as water depth, currents, rates of sediment resuspension and deposition, and mode of transport through the water column will also contribute to the concentration of contaminants in the surficial sediments. Therefore, to minimize the size of this pool of contaminants, both the rate of discharge of produced water and its content of toxic substances should be limited. Again, we have insufficient data to suggest critical values for these parameters. We should add that, in the Buccaneer Field, no adverse effects were found which could be ascribed to the presence of contaminants in the surficial sediments.

There are at present no mandated analytical procedures for the analysis of the organic toxic pollutants, although proposed methods based upon gas chromatography (GC), high-performance liquid chromatography (HPLC), and combined gas chromatography - mass spectrometry (GC-MS) have been described (Federal Register, December 3, 1979). It was indicated in the recently issued Consolidated Permit Regulations that GC-MS would be the method of choice in most instances (Federal Register, May 19, 1980). With the detection limits cited for the proposed GC-MS method, only five organic toxic pollutants would have been reported: acenaphthylene, benzene, ethylbenzene, naphthalene, and toluene. We have in fact found additional organic toxic pollutants at lower concentrations, and we have also found other toxic substances which are not on the formal list of organic toxic pollutants. The priority pollutants were chosen during a consideration of effluents from a wide range of different industries. Most of them will not be found in discharges from offshore production platforms. Conversely, there are toxic substances that we have identified in the effluents which are not on the list of priority pollutants. A more appropriate list of substances to be monitored could be prepared for this industry. This revised list could include alkylated homologs of the aromatic hydrocarbons, since they are similar in physical properties and toxicity to the parent compounds. We should also point out that, of the methods of analysis listed above, only GC-MS provides sufficient sensitivity and specificity for characterizing these complex effluents.

SECTION 3

BACKGROUND

Debate over the environmental effects of offshore oil production has been continuing ever since the concept of drilling at sea was introduced. On the one hand, there are those who wish to protect the environment from unreasonable assault and, on the other hand, there are pressures to produce more oil and to produce it as inexpensively as possible. In the United States, the latter concern has been compounded by a realization of the problems which can result from overdependence upon imported oil.

For a reasonable debate to proceed to a resolution of differences of opinion, reliable and appropriate data must be made available. Many studies have been made of the environmental effects of major oil spills and well blowouts. Much data has been obtained concerning the toxicity of oil and its components on marine organisms. However, at the inception of this project, little was known about the environmental effects of routine offshore oil production.

To place our research in a proper perspective, we are first reviewing the existing literature on other inputs of petroleum hydrocarbons to the marine environment. This is followed by a discussion of the effects of oil upon marine organisms. Finally, we provide a brief review of biogenic hydrocarbons which must be distinguished from petroleum hydrocarbons.

3.1. MAJOR SPILLS

Major oil spills have resulted from tanker wrecks and drilling accidents.

3.1.1. Tanker Wrecks

One of the first major oil spills to receive world-wide attention from the press and scientific community alike, was the stranding of the "Torrey Canyon" in the western approach to the English Channel on March 18, 1967. During March and April her 29.4 million gallon load of Kuwait crude was released, and much of it reached the beaches of England and France. Unfortunately, conclusions on the biological effects of this well documented spill remain somewhat confused since large quantities of toxic dispersants were used during the clean-up process (Nelson-Smith, 1973).

When the oil barge "Florida" ran aground just off Little Island, West Falmouth, Massachusetts in 1969, approximately 175,000 gallons of Number Two fuel oil leaked into Buzzards Bay and the adjacent Wild Harbor Marsh. Scientists from the nearby Woods Hole Oceanographic Institution were able to study the incorporation of polluting hydrocarbons into the marsh ecosystem.

Massive kills of marine and marsh life were reported immediately after the spill and oysters and scallops were found to be contaminated with fuel oil (Blumer et al., 1970). Analyses of sediments and marsh organisms collected a year later showed an accumulation of petroleum hydrocarbons. Chromatograms of pentane extracts revealed the loss of lower boiling components of the oil, and the accumulation of cyclic and aromatic hydrocarbons (Burns and Teal, 1971; Blumer et al., 1973). Sediments examined two years after the spill still demonstrated the persistence of fuel oil hydrocarbons (Blumer and Sass, 1972).

When the tanker "Argo Merchant" went aground near Nantucket Island, Massachusetts on December 15, 1976 more than 7.7 million gallons of number six fuel oil were lost. Immediately after the wreck scientists from throughout the U.S. began to make an assessment of the impact of spilled oil on the ecology of the area. Analysis of sediments collected within two months of the spill did not indicated the presence of oil in significant quantities, except within 10 miles of the bow section, where concentrations up to 100 ppm were measured in a few samples. There was evidence of oil contamination in fish, shellfish, ichthyoplankton, and other zooplankton in the area of the spill. Benthic filter-feeders such as mussels, scallops and quahogs, however, did not then show an accumulation of hydrocarbons (Grose and Mattson, 1977).

In the largest tanker disaster recorded, the "Amoco Cadiz" released 65 million gallons of crude oil and bunker fuel just 1.5 km from the northwest coast of France. During the 15 days following the wreck on March 16, 1978, 140 km of the Brittany coast was heavily impacted by oil. Heavy mortalities of some intertidal organisms, birds, and other marine organisms were observed as well as incorporation of oil in sediments up to 70 cm in depth (Hess, 1978). Just one year after the wreck, however, a return survey of the area by biologists from the U.S. and France reported a substantial increase in Odum's diversity index and attendant recolonization of coastal areas (Cross, 1979), thus indicating movement toward ecological recovery of the damaged area.

Toward the end of 1979, a collision occurred between the tanker "Burmah Agate" and the freighter "Mimosa" in the Gulf of Mexico off Galveston, Texas. Some of the tanker's cargo spilled into the sea, but much of it burned over a period of several weeks. The environmental impact of this incident is still being assessed.

3.1.2. Drilling Accidents

The estimated total volume of oil spilt from the blow-out (January, 1969) of Union oil well A-21 in the Santa Barbara Channel was in excess 3.25 million gallons. While the volume is certainly comparable to that spilt by tankers, it appears that the ecological effects were not as substantial. Phytoplankton productivity (esential to any marine ecosystem) after the blow-out was well within the established pattern observed under normal conditions of nutrient availability, and breeding among the copepod *Labidocera trispinosa* was successful, thus indicating minimal ecological stress (McGinnis, 1971). "Blooms" of a tunicate copepod were also observed as well as a normal variety and abundance of fish eggs and larvae (Straughan, 1970). It has been argued, however, that had the sophisticated analytical chemical techniques used in evaluating other spills been applied to the Santa Barbara spill a more serious picture of the ecological damage may have been obtained (Easton, 1972).

The largest oil spill due to a drilling accident was the Ixtoc-I blowout on June 3, 1979 on the Mexico continental shelf of the Gulf of Mexico. Non-toxic dispersants were used to prevent oil from reaching Mexican beaches (except on a few occasions), but some South Texas beaches were heavily impacted until the prevailing currents changed direction in the fall. Although the well was not capped until March of 1980, only small amounts of additional oil reached the Texas coast. The ecological effects of this incident are still being studied.

3.2. OTHER SOURCES OF OIL

3.2.1. Natural Seeps

The presence of oil seeps in the Santa Barbara Channel (California) has been documented as early as 1543 (Easton, 1972). In order to assess the consequences of this geological phenomenon, a series of field surveys was conducted from 1972 through 1974. Coal Oil Point, an area of natural oil seepage in the Santa Barbara Channel, was compared with control sites that were not chronically exposed to natural oil seepage. The studies were designed to encompass most segments of the environment, most invertebrate groups, and most habitat types. Species examined were sedentary (non-migratory) to ensure that speciemens had actually been exposed to conditions in this area. Some of the most significant results were (Straughan, 1976):

> (1) Animals are inhabiting areas of Coal Oil Point which have relatively high levels (up to 9%) of petroleum hydrocarbons in the sediments;
>
> (2) The distribution of petroleum hydrocarbons is patchy throughout the environment in terms of time, locations, and tissue type;
>
> (3) Total hydrocarbon values alone cannot be used as indicators of petroleum contamination due to the variability in composition of both petroleum and biogenic hydrocarbons;
>
> (4) No malformations were observed in the thousands of organisms examined from Coal Oil Point; and
>
> (5) Specimens of abalone (*Haliotis* sp.), sea urchin (*Stronglylocentrotus purpuratus*), and mussel (*Mytilus californianus*) from Coal Oil Point are more tolerant of exposure to Santa Barbara crude oil and seem to be hardier in terms of survival and adjustment to laboratory conditions than animals from control locations .

It has been estimated that the petroleum contribution of natural seeps is 0.6 million tons annually (Wilson, *et al.*, 1973). While these figures have been criticized as being too high (Blumer and Sass, 1972), petroleum geologists generally agree that a more accurate figure would be extremely difficult to estimate.

3.2.2. Anthropogenic Sources

Other sources of oil in the sea include those from shipping operations, oil ports and terminals, offshore drilling and production, refineries, runoff, and sewage. The only source of continuous low-level chronic pollution which had received any great amount of attention prior to our study was refinery effluents (Cowell, 1976). However, these results are not comparable to those obtained for effluents from offshore production platforms since the toxicity of the refinery effluents is not attributable solely to oil (Baker, 1975).

3.2.3. Relative Significance

Several attempts have been made to provide an inventory of the various inputs of oil to the marine environment. In most of these estimates, offshore production is credited with only a small proportion of the total oil input. Wilson *et al.* (1973) estimated that 80,000 metric tons per annum derived from this source. The National Academy of Sciences (1975) evaluated these data and indicated a probable range of input to be 80,000 to 150,000 metric tons per annum. They concluded also that the total oil input was approximately 6.113 million metric tons, so that offshore production would account for 1.3-2.5% of the total input (Table 1).

Oher estimates are difficult to compare. Travers and Luney (1976) estimated that only 0.006% of the oil handled during offshore operations was spilled (compared with 0.016% of the oil carried by tankers). The Massachusetts Institute of Technology Study Group on Criticial Environmental Problems reported that, along with ocean shipping and accidents, offshore drilling may have accounted for a "significant" portion of about 2 million tons of oil introduced into the oceans annually (Wilson, 1970). McCaslin (1972) calculated that 1,500 bbl of oil per year were spilled in U.S. waters and that 10,000 metric tons per year were spilled world-wide.

It is clear that a global estimate of oil input to the sea from offshore operations is difficult, if not impossible, to obtain. Moreover, since the contribution of oil from natural seeps is particularly difficult to determine, the relative amount of oil from offshore production losses is even more elusive. Most estimates agree that this input is relatively low in comparison to the total global input of oil to the sea. The question which remains unanswered is whether a significant quantity of oil is released in areas (such as the Gulf of Mexico) where intensive offshore production is taking place.

3.3. PREVIOUS ENVIRONMENTAL STUDIES

While the literature on oil spills and related topics is voluminous, it has been criticized along two major lines (National Academy of Sciences, 1975). To accurately assess the ecology of an area not only requires a great deal of funding for a short-term intensive study, but also requires information gained form long-term investigation of several facets of that system.

TABLE 1. BUDGET OF PETROLEUM HYDROCARBONS INTRODUCED INTO THE OCEANS[a]

	Input Rate (million tons per year)	
	Best Estimate	Probable Range
Natural seeps	0.6	0.2-1.0
Offshore production	0.08	0.08-0.15
Transportation		
LOT tankers	0.31	0.15-0.4
Non-LOT tankers	0.77	0.65-1.0
Dry docking	0.25	0.2-0.3
Terminal operations	0.003	0.0015-0.005
Bilge bunkering	0.5	0.4-0.7
Tanker accidents	0.2	0.12-0.25
Nontanker accidents	0.1	0.02-0.15
Coastal refineries	0.2	0.2-0.3
Atmosphere	0.6	0.4-0.8
Coastal municipal wastes	0.3	-
Coastal industrial wastes	0.3	-
Urban runoff	0.3	0.1-0.5
River runoff	1.6	-
TOTAL	6.113	

[a] From National Academy of Sciences (1975).

In all of these cases funding has limited the scope and nature of the work (Michael, 1977). It is probable too that long-term studies may uncover minor alterations which may seem insignificant in the short-term but may be cumulative and drastic over a long period of time.

While ecological effects of many major oil spills have been studied intensively by groups of scientists from various disciplines and the literature generated has been incisive, informative, and extensive, the same cannot be said of studies of the ecological impact of offshore drilling and production activities. Most of the literature to date has been fragmentary in that individual studies have focussed narrowly on one biological, chemical, physical, or geological facet of the total ecosystem possibly affected by petroleum activities. In fact, isolated studies of the effects of oil on a single component of an ecosystem which do not have the benefit of comparison with changes in parameters of other components of the ecosystem (e.g., water column hydrocarbon content, sediment characteristics, wind and current variation, seasonal planktonic variation) approach irrelevance with respect to a comprehensive assessment.

3.3.1. The Offshore Ecology Investigation

Due to the paucity of data on the environmental impacts of offshore petroleum operations, the Gulf Universities Research Consortium (GURC) conducted an offshore ecology investigation (OEI) between June 1972 and January 1974.

Notable of this study and possibly the first for an environmental project, was the synoptic multidisciplinary data acquisition and synthesis. This type of approach has been called for by various commentators (National Academy of Sciences, 1975; Farrington et al., 1976) and is demanded by the complexity of environmental problems.

The OEI study was conducted in Timbalier Bay, Louisiana and the adjoining near-shore shelf region. In addition, samples were obtained in the vicinity of platforms experiencing drilling or prolonged intensive production activity. Sampling sites were chosen so as to minimize the impact of the Mississippi River and yet to provide an ecologically contiguous area, and the duration of the study was sufficiently long-term to detect persistent impacts as well as short-term variations. Conclusions based on the data generated are (Morgan et al., 1974):

(1) concentrations of trace metals and hydrocarbons are sufficiently low (less than 11 ppb in the water column) to present no known persistent biological hazards. In fact, hydrocarbon concentrations in the water column, sediments, and living organisms were of the same order of magnitude as those reported in the literature for the Atlantic Ocean or the Gulf of Mexico;

(2) the region of sampling sites is highly productive from a biological standpoint, more than other regions studied in the eastern and open Gulf of Mexico;

(3) natural phenomena such as seasonality, floods, upwelling, and turbid layers have a much greater impact upon the ecosystem than do petroleum drilling and production activities; and

(4) Timbalier Bay has not undergone significant ecological change as a result of petroleum drilling and production since just prior to 1952 when more limited baseline data were gathered.

3.3.2. Other Studies

Other investigations have usually focused upon sediments in the vicinity of oil production operations since this environmental compartment was postulated to be a repository for residues of discharged oil. One offshore area studied was Lake Maracaibo, in the state of Zulia, Venezuela. Oil production has been localized in the northwest quadrant of the lake for 40 years, so appropriate control stations were chosen in other areas of the lake. The saturated fraction of sediment samples ranged from 250 ppm to 3700 ppm of hydrocarbons, while the aromatic fraction ranged from 430 ppm to 6600 ppm. The quantity of organic material extracted decreased as the distance from the production zone increased (Bean *et al*., 1977).

Brooks *et al*. (1977) have reported data for the light hydrocarbon content of discharges from a production platform off the Louisiana coast. Measurements of the C_1 to C_4 hydrocarbons showed a 20-fold increase in Louisiana shelf waters over open ocean levels of these substances, and it was calculated that 450 metric tons per year of C_5 to C_{10} hydrocarbon were being added to these waters each year.

A comprehensive (but brief) study of the environment surrounding a drilling rig on the South Texas Continental Shelf was made in 1976 as a part of an overall study of this area by the Bureau of Land Management (1977). This agency also inaugurated a study of the Gulf of Mexico off Louisiana to evaluate the impact of offshore production during the time that we were conducting our studies.

3.4. EFFECTS OF OIL UPON MARINE ORGANISMS

The complexity of crude oil, being a mixture of hydrocarbons, non-hydrocarbon compounds containing oxygen, sulfur, and nitrogen, and many trace metals, in large part complicates the assessment of its effects on marine organisms. In addition, oils from different geographic locations can be very different in composition and therefore in toxicity. The deleterious effects of crude oil on living organisms may be generalized into five main categories:

(1) acute toxicity,
(2) direct coating and asphyxiation,
(3) disruption of behavioral activities,
(4) changes in biological habitat, and
(5) carcinogenicity.

3.4.1. Acute Toxicity

Laboratory bioassays have been used to quantitate the toxicity of crude and refined oils to marine life. Recently, two objectives in this type of testing have emerged. One is the use of toxicity data to determine and compare toxicity of individual components of a certain oil (*e.g.*, naphthalenes *vs*. cycloalkanes) or relative toxicity of various oils (*e.g.*, Kuwait *vs*. South Louisiana crude). The second is the use of acute toxicity data to compare the sensitivity of different species or life stages of that species to the individual components or specific oils (Rice *et al*., 1977). Problems of comparing and interpreting different laboratory studies arise due to dissimilarity in experimental conditions and the lack of measurement of hydrocarbon concentrations (Moore and Dwyer, 1974).

Using bioassays, investigators have shown a high correlation between toxicity of specific oils and dispersants and the quantity of light aromatics which that substance may impart to the test medium (Nelson-Smith, 1970; Moore and Dwyer, 1974). The most prominent low-boiling aromatics found in oiled test waters are the methylnaphthalenes, presumably due to the relatively high water solubility of the diaromatics.

In an attempt to normalize reported toxicity data, Moore and Dwyer (1974) have estimated the composition of various test oils reporting soluble aromatic derivatives (SAD) as a basis for comparison. In addition, they have proposed grouping of organisms on the basis of life style to further simplify data comparison.

3.4.2. Direct Coating and Asphyxiation

These harmful effects of oil can be ascribed to its viscous and hydrophobic physical properties. The oiling of birds' feathers as well as consumption of oiled food accounts for mortality among exposed animals. Fish coming into direct contact with oil may likewise be asphyxiated due to coating of gill tissue, thus preventing gas exchange.

3.4.3. Disruption of Behavioral Activities

Sublethal behavioral changes have been observed. For example, Takashi and Kittredge (1973) obtained evidence for interferences with chemotactic feeding and mating responses in many organisms.

3.4.4. Changes in Biological Habitat

Oil affects various biological habitats differently. Open ocean habitats covered by a surface slick probably are least affected due to the mobility of the slick and extensive dissolution and evaporation related to water depth, currents, and prevailing winds. Intertidal areas impacted by oil generally suffer tarry surface coatings due to loss of lighter hydrocarbons. This loss, accelerated by intermittent immersion and exposure, has the net effect of reduced toxicity. However, since the lighter aromatics are easily evaporated under these conditions (National Academy of Sciences, 1975), estuaries, bays and marshlands may suffer the most extensive damage from spilled oil. The sheltered nature of these habitats means a drastic reduction in energy available for certain physical processes: dissolution, evaporation, emulsification, and sediment interaction, resulting in longer exposure of the ecosystem to the oil.

3.4.5. Carcinogenicity

In addition to the toxic light aromatics, high-boiling polycyclic aromatic hydroarbons are found in crude and refined oils. These compounds have long been known to induce formation of neoplasms in test animals. Certain histopathologic findings in bottom-feeding fishes and eels thought to be a result of exposure to refinery effluents and oiled sediments, respectively (Russell and Kotin, 1956), were probably due to exposure to oil-derived carcinogens. Since these compounds have been shown to be accumulated (Scaccini et al., 1970) and to cause disease in marine organisms, the possibility of human exposure to oil-derived carcinogens from commercial fish consumption is a justifiable concern.

3.5. HYDROCARBONS IN THE MARINE ENVIRONMENT

3.3.1. Seawater

Organic compounds are introduced into seawater from many and varied sources. The variability in the nature of marine organic matter can provide tags for recognizing specific water masses for long time periods. Blumer (1970) identified the organic compounds present in the pentane-soluble fraction of local near-shore surface water. Straight-chain hydrocarbons from C_{14} to C_{33}, with maxima at C_{25} to C_{28}, were reported. No odd-even predominance was observed. Isoprenoid hydrocarbons, pristane and phytane, were also represented. Similar results were reported for coastal and open seawaters off the coasts of France and west Africa (Barbier _et al_., 1973). The concentrations in these samples varied from 10 to 140 ppb, with a maxima at n-C_{27} to n-C_{30}. For Atlantic Ocean water, the median concentration of nonvolatile hydrocarbons was 4 ppb, with values ranging from 1.3 to 13 ppb (Brown and Huffman, 1976). Concentrations of hydrocarbons in the eastern Gulf of Mexico and the Caribbean Sea ranged from traces to 75 ppb with a maximum n-alkane content between C_{15} and C_{20} (Iliffe and Calder, 1974).

The organic constituents of river water have been identified as normal alkanes (C_{15} to C_{31}), alkyl naphthalenes, alkyl anthracenes or phenanthrenes, pyrene, fluoranthrene, and phthalates with concentrations ranging from 0.05 ppb for pyrene to 1 ppb for bis(diethylhexyl) phthalate (Hites and Biemann, 1972). Petroleum ether extracts of San Francisco Bay water contained 2.5 to 102 ppb of cyclic and acyclic hydrocarbons such as n-alkanes, steranes, and unsaturated hydrocarbon (Simoneit _et al_., 1973).

Most of the organic compounds in water occur either in particulate residues or in the surface microlayer. Particulate petroleum residues have been collected from the Gulf Stream, Sargasso Sea, and the Caribbean Sea, as well as the Mediterranean Sea and the eastern North Atlantic Ocean (Horn _et al_., 1970; Levy and Walton, 1976). Normal alkanes in surface microlayer samples from the Gulf of Mexico ranged from C_{16} to C_{27}; however, the predominant compounds were methyl branched alkanes ranging in chain length from C_{15} to C_{35} and cycloalkanes (Ledet and Laseter, 1974).

Since the hydrocarbons of most marine organisms are dominated by a few compounds (see following sections), it can be expected that seawater containing only biogenic compounds would also have a limited diversity of hydrocarbon composition. However, if the range of hydrocarbons in a water sample is complex, then it is likely that these compounds are petroleum-derived. This conclusion would be substantiated by the presence of aromatic hydrocarbons.

3.5.2. Bacteria

Uncharacterized or partially characterized mixtures of alkanes have been reported for _Sarcina lutea_ (Albro and Huston, 1964), _Desulfovibrio desulfuricans_ (Davis, 1968), _Vibrio marinus_ (Oro _et al_., 1967), _Escherichia Micrococcus lysodeikticus_, _Rhodopseudomonas spheroides_, and _Rhodospirillum_ *rubrum* (Han *et al.*, 1968), and *Pseudomonas shermanii*, *Clostridrium*, *Chlorobrium*, and *Rhodomicrobium* (Han and Calvin, 1969). It was generalized that most photosynthetic bacteria contain predominantly medium length (C_{14} to C_{20}) hydrocarbons, while non-photosynthetic bacteria have higher molecular weight (C_{26} to C_{30}) hydrocarbons (Albro, 1976). The hydrocarbons present were usually alkanes, monounsaturated alkanes with a double bond in the middle, or *iso* or *anteiso* methyl branched alkanes (Albro, 1969, 1976).

3.5.3. Plankton and Algae

Hydrocarbons other than squalene are generally trace constituents in marine animals. They may, however, be major components of marine algae. Analysis of the alkane content of 12 species of northeast Atlantic intertidal zone seaweeds, one species of pelagic seaweed, three species of cultured algae, and a mixed marine plankton sample resulted in a hydrocarbon content of 10-20 ppm with an insignificant odd-carbon predominance. All the algae analyzed had a concentration maximum in their alkane profiles at C_{15} or C_{17}, a minimum between C_{19} and C_{21}, and a secondary maximum near C_{27} to C_{30}. Based on this information, the algae were placed in one of two categories depending on their primary concentrations maximum. In the red and green algae, n-heptadecane dominated while, in the brown algae, n-pentadecane predominated (Clark and Blumer, 1967).

An algal mat sample from the Texas Gulf coast contained hydrocarbons ranging from n-C_{15} through n-C_{31} with only small amounts above n-C_{23} (Oro´ *et al.*, 1967). The major component of the mat samples was n-heptadecane. This compound also dominated in the blue-green algae *Anacystis nidulans*, *Nostoc muscorum*, *Phormidium luridum*, and *Chlorogleae fritschii* as well as in the green algae *Spirogyra* and *Chlorella* (Han *et al.*, 1968a,b). Samples of blue-green algae and green algae, cultured in the laboratory or collected from seawater, were shown to contain alkanes in the range C_{14} to C_{23} with no odd-carbon dominance if n-heptadecane is ignored (Han and Calvin, 1969; Winters *et al.*, 1969; Botello and Mandelli, 1978). However, a few species were reported to contain a bimodal distribution of aliphatic hydrocarbons with maxima at n-C_{17} and n-C_{27}, and significant amounts of n-C_{23}, n-C_{27}, and n-C_{29} olefins and paraffins (Gelpi *et al.*, 1970).

Terpenoid hydrocarbons, derived from isopentenyl pyrophosphate, have been reported in a wide variety of marine organisms. Pristane (2,6,10,14-tetramethylpentadecane) is the major hydrocarbon in copepods and zooplankton (Blumer *et al.*, 1963, 1964; Clark and Blumer, 1967). Crude pristane has been shown to contain isomeric C_{19} monoolefins, which originate in the phytol digested by zooplankton (Blumer and Thomas, 1965a,b; Avigan and Blumer, 1968). Di- and triolefinic derivatives of pristane (2,10- and 5,10-dienes and the 2,6,10-triene) were also isolated from zooplankton (Blumer *et al.*, 1969). Phytane and squalene have been reported as algal hydrocarbons in a limited number of cases (Oro´ *et al.*, 1967; Gelpi *et al.*, 1970; Halsall and Hills, 1971; Paoletti *et al.*, 1976).

Other branched, saturated alkanes, include the 7- and 8-methylheptadecanes present in blue-green algae (Han *et al.*, 1968a,b; Han and Calvin, 1969).

Based on this background, it has been shown that pelagic *Sargassum* weed was contaminated with petroleum, since samples showed a series of alkanes from C_{16} to C_{30} and phytane (Burns and Teal, 1973).

The monounsaturated C_{15} to C_{12} alkenes have been demonstrated to be important components of some phytoplankton (Winters *et al*., 1969). Three isomeric heptadecenes were isolated from algae, and the double bond locations were established as being in the 3-, 5-, and 7- positions (Blumer *et al*., 1971; Youngblood *et al*., 1971). Recently it was reported that green algae (Chlorophyceae) contain appreciable amounts of an n-C_{27} monoene (Paoletti *et al*., 1976)

Diolefins were reported to be major components of the algae *Botyrococcus braunii* and *Anacystis montana* with the identification of 1,18-heptacosadiene, 1,20-nonacosadiene, and 1,22-hentriacontadiene (Gelpi *et al*., 1968; Knights *et al*., 1970).

However, the predominant hydrocarbons of most marine algae are polyunsaturated, such as the all-*cis*-3,6,9,12,15,28-heneicosahexaene (HEH) (Lee *et al*., 1970). The compound has been reported in representatives from the algal classes Bacillariophyceae, Dinophyceae, Cryptophyceae, Haptophyceae, and Euglenophyceae (Blumer *et al*., 1970). A hydrogenation product, n-heneicosane, of HEH was found in *Rhizosolenia setigara*, and the corresponding tetraolefin was a minor component of *Talassioseria fluviatilis* (Blumer *et al*., 1971).

Compounds related to HEH, 1,6,9,12,15-heneicosapentaene and 1,6,9,12,15,18-heneicosahexaene, have been reported in the brown algae *Fucus vesiculosus* (Halsall and Hills, 1971). Other polyunsaturated olefins, found in various algae, include the all-*cis*-4,7,10,13-nonadecatetraene, the all-*cis*-3,6,9,12,15-nonadecapentaene, the all-*cis*-3,6,9,12,15-heneicosapentaene, and a compound tentatively identified as all-*cis*-1,4,7,10,13,16-nonadecahexaene (Youngblood *et al*., 1971; Youngblood and Blumer, 1973).

Since most hydrocarbon are less dense than seawater, it is possible that these are important in providing buoyancy to marine organisms. For example, squalene which cannot be oxidized through the cholesterol pathway has been ascribed such a role (Sargent *et al*., 1976).

Certain compounds such as n-alkanes and olefins are more abundant in vegetative than in reproductive tissue in phytoplankton. Polyunsaturated hydrocarbons such as HEH, however, occur exclusively in the reproductive tissue suggesting a possible correlation between reproductive chemistry and the olefin content of benthic and planktonic marine alga (Youngblood *et al*., 1971). For example, mature female receptacles of *Fucus vesiculosus* have a lower polyolefin content than in a younger specimen. Also, the polyolefin content of developing receptacles is higher than that of sterile thallus, but it decreases again with increasing maturity of the fruiting bodies suggesting considerable hydrocarbon recycling (Youngblood and Blumer, 1973).

It has alo been suggested that the sex ratio of laboratory reared *Calanus helgolandicus* depends on the composition of algal food (Paffenhofer, 1970).

Youngblood and Blumer (1973) suggested that the percentage of males could be correlated with the predominance of HEH in the algal food fed to the nauplii.

These recent discoveries suggest a deeper involvement of straight-chain hydrocarbons in cell biochemistry than was previously considered. However, the mode of biosynthesis or the function of many of these compounds remains unknown.

3.5.4. Invertebrates

Hydrocarbons isolated from marine organisms grown in water culture under conditions which avoid contamination by petroleum hydrocarbons are not very diverse and have a limited boiling range (n-C_{12} to n-C_{22}) (Farrington et al., 1976). For example, the crustacean Ligia oceanica has surface waxes composed of n-alkanes from C_{14} to C_{33} and pristane (Hamilton et al., 1975). Shrimp and squid from the Gulf of Mexico both contained pristane; however, shrimp have very low concentration of C_{15} and C_{17} paraffins with their maximum concentration at C_{31}. The alkanes C_{15} and C_{17} dominate in the squid samples (Giam et al., 1976). As a part of a baseline study, oysters from Campeche, Mexico were examined for their hydrocarbon content. They showed n-alkanes in the C_{14} to C_{32} range with a predominance of C_{23} and C_{21} compounds in all the samples analyzed (Bottello and Mandelli, 1978). The naturally occurring hydrocarbon content of marine mussels is approximately 0.33% with the major components being pristane, eicosene, and heneicosahexane (Lee et al., 1972).

In contrast to the odd-carbon predominance exhibited for representatives of the phyla Mollusca and Arthropoda, the n-alkane distributions of Porifera (sponges) and Coelenterata (corals) revealed very little odd-even preference in the C_{24} to C_{34} range (Koons et al., 1965). Many of these organism are identified in the algal mat associated with barnacle shells such as those seen on the legs of offshore production platforms (Fortheringham, 1977; Martin, 1978).

Mussels have been proposed as a test organism for monitoring long-term hydrocarbon pollution in marine waters. Mytilus edulis rapidly assimilated labeled hydrocarbons or fuel oil and, after transfer to seawater, they discharged most of the hydrocarbons (half-life; 2.7 to 3.5 days) (Lee et al., 1972; DiSalvo et al., 1975; Fossato and Canzonier, 1976). Oysters (Crassostrea virginica), clams (Rangia cuneata), fish (Fundulus similus), and shrimp (Penaeus aztecus) also accumulated a wide variety of hydrocarbons when exposed to oil-contaminated seawater. After return to oil-free water, these animals released the accumulated hydrocarbons from their tissues. However shrimp and fish, which can metabolize hydrocarbons, released them more rapidly than clams or oysters, which apparently lack the detoxifying enzymes (Stegeman and Teal, 1973; Neff et al., 1976).

Molluscs from various locations have been examined for their hydrocarbon pollutant content. Mussels (Mytilus edulis and M. californiaus) from Puget Sound and the Strait of Juan de Fuca, clams (Mercenaria mercenaria) from Narrangansett Bay, and oysters (Crassostrea virginica) from Galveston Bay all exhibited a complex mixture of hydrocarbons which resembled the distributions found in crude oil as well as the abiogenic acyclic and aromatic compounds

(Ehrhardt, 1972; Clark and Finley, 1973; Farrington and Quinn, 1973). Other molluscs have been shown to contain polycyclic aromatic hydrocarbons or to release these compounds after exposure to clean water (Bravo et al., 1978; Dunn and Stich, 1976).

3.5.5. Vertebrates

Gas chromatographic analysis of herring oil revealed the presence of aliphatic hydroarbons from C_{14} to C_{33}, with high concentrations of n-C_{17}, n-C_{19}, n-C_{25}, n-C_{27}, and n-C_{29}. The terpenoids pristane and squalene were also present (Lamberten and Holman, 1963). Pristane and it olefinic analogs have been identified in the oils of various freshwater and marine fish such as *Pomolobus* sp. (alewife), *Cetorhinus maximum* (basking shark), *Gadus* sp. (cod), and *Aplodinotus grunniens* (freshwater drum), as well as in the sperm whale (*Physeter catodon*) (Blumer and Thomas, 1965; Blumer et al., 1969; Ackman, 1971). The hydrocarbon patterns of various fish from the Gulf of Mexico have also been examined. The sand seatrout, longspine porgy, and the flounder have bimodal distributions of aliphatic hydrocarbons and a high pristane content. These benthic fish oils are composed primarily of the n-alkanes C_{15}, C_{17}, and C_{25} through C_{35}. On the other hand, the wenchman has n-C_{15} and n-C_{17} as the dominant hydrocarbons with trace amounts of other compounds (Giam et al., 1976).

Hydrocarbons in vertebrates are thought to arise from their diet (Blumer, 1967). This was evident in studies of wild codling which were fed cod liver oil containing crude oil. Within six months, the alkane pattern in the liver lost its marked odd-even preference, and the maximum decreased from C_{29} or C_{31} to C_{26} (Hardie et al., 1974). It has been postulated that hydrocarbons are formed by the decarboxylation of fatty acids which would account for the dominance of odd-chain hydrocarbons. However, a biosynthetic pathway for the formation of hydrocarbons of chain lengths greater than C_{26} has yet to be found in marine vertebrates (Sargent et al., 1976).

3.5.6. Sediments

Geologists have studied sedimentary material from various locations in their quest for the origin of petroleum. Examination of recent marine sediments from the Gulf of Mexico revealed the presence of normal paraffin hydrocarbons ranging from C_{12} to C_{32}. The dominant hydrocarbons were nonacosane (C_{29}) and hentriacontane (C_{32}), and the muds showed a marked odd-even preference (Stevens et al., 1956; Evans et al., 1957). Similar distributions have been seen in sediments from San Francisco Bay, California (Kvenvolden, 1962), Tarpaulin Cove Massachusetts (Clark and Blumer, 1967), Lake Zug, Switzerland (Giger et al., 1974), and Terminos Lagoon, Campeche, Mexico (Bottello and Mandelli, 1978), in addition to lacustrine and subtropical lagoonal/tidal flat sediments (Brooks et al., 1976). Some recent sediments do not contain phytane, suggesting a geochemical origin for phytane (Blumer and Snyder, 1965).

While sediments exhibit a marked odd-even preference (OEP), source rocks and shale from various ancient sediments have an OEP ratio close to unity (Bray and Davis, 1961; Meinschein, 1961). Examination of source rocks has led to the postulate that petroleum is generated by thermal, nonbiological processes, and that it migrated through faults and fractures (Philippi, 1965). Examination of aliphatic hydrocarbon and fatty acids in a salt marsh, however, showed a marked change in the OEP values from 3.2 in the surface sediments to 1.1 in the bottom core (24 cm). This was postulated to occur through *in situ* microbial activity by modification of fatty acids and deposition of branched-chain compounds (Johnson and Calder, 1973).

Sediment samples taken from various locations which have a terrigenous input can be compared to samples from locations with a marine input. For example, cores from the continental slope of the eastern Atlantic ocean showed a low OEP ratio in the uppermost 15 cm (1.5) suggesting a crude petroleum input, but the lower two sections showed ratios similar to those seen in terrestrial aquatic sediments (Gaskell *et al*., 1975). Sediments deposited in a lake after 1880 showed a marked increase in petroleum-type hydrocarbons (Wakeham and Carpenter, 1976). Similarly, sediments from Boston Harbor, Massachusetts and Lake Zug, Switzerland which have areas of predominantly petroleum input and areas of predominantly biogenic input can be easily contrasted with respect to their hydrocarbon content (Shaw, 1973; Giger *et al*., 1974). In the Gulf of Mexico, samples from the Mississippi coast have an even distribution of alkanes, while sediments from the Florida coast contain mainly odd-carbon high molecular weight alkanes (Gearing *et al*., 1976; Lytle and Lytle, 1976).

Analysis of sediment samples has demonstrated a complexity of the polycyclic aromatic hydroarbon (PAH) fraction. The principal series, unsubstituted hydrocarbons and alkyl derivatives, occurs over a wide molecular weight range. The minor series, interpreted as napthenologs and thienologs of the basic PAH series, also cover a wide carbon range, several possible origins for the PAH mixture have been postulated. These included biochemical, early diagensis, and pyrolysis at various temperatures. A biochemical origin for the sedimentary PAH fraction would lead to simple mixture of compounds which are not chemically complex. However, the low abundance of linear systems (anthracene, *etc*.), the predominance of unsubsituted hydrocarbons, the thienologs, and the great overall complexity are more characteristic of a thermal origin. Early diagensis would favor a high degree of alkyl substitution and would not be very likely to be deposited widely in the environment. Pyrolysis at high temperatures (automotive engines and domestic heating) favors unsubstituted aromatics. Therefore a pyrolytic origin at intermediate temperatures was suggestd. A wood pyrolysate had molecular weight distribution patterns similar to those seen in sediment samples (Giger and Blumer, 1974; Youngblood and Blumer, 1975; Blumer and Youngblood, 1975; Blumer *et al*., 1977).

Cores from two locations in the Grosser Ploner Sea (Germany), one obtained near a railway station and the other from a virgin area of beach, showed a substantial increase in PAH content after 1920 (Grimmer and Bohnke, 1975). Examination of cores from Buzzards Bay, Massachuetts revealed that the concentrations of PAH from sections dated after 1910 greatly exceed those concentrations from sections dated around 1850 (Hites *et al*., 1977). All the authors concluded that the major source of PAH in these locations was anthropogenic combustion.

SECTION 4

THE BUCCANEER GAS AND OIL FIELD STUDY

4.1. RATIONALE

The foregoing literature survey reveals many gaps in our knowledge of the environmental effects of offshore activities. Given the time and the level of funding available for this study, it was impractical to gather sufficient data to assess the overall impact of these activities, even in a limited geographic region such as the Gulf of Mexico. The approach selected was to perform an intensive study of a single offshore field so that we could fully document whatever effects might be ascribed to its operations. It was fully realized at the outset that the findings of such a study might not be legitimately applied by extrapolation to other fields in determining the overall effects of offshore operations in the Gulf of Mexico. It was anticipated, however, that sufficient knowledge might be obtained to recognize the parameters which might be responsible for the individual effects so that they could be monitored and controlled.

The area selected for study was the Buccaneer Field located 50.5 km south of Galveston, Texas (a map of the region is given in the editorial section preceding this report). Rationale for selection of this field included:

(1) the field has been in production for about 15 years, which time had allowed full development of the oil field associated climax marine communities;

(2) it is isolated from other fields, which facilitated the selection of an unaltered area (for comparison) within a reasonable distance of the field;

(3) it produces both oil and gas that create a major portion of the pollutants from marine mineral extraction;

(4) its location simplified logistics and reduced the cost of the research; and

(5) the Texas offshore area has not as yet been fully developed for gas and oil production but will probably experience accelerated exploitation in the near future.

4.2. THE BUCCANEER FIELD

A description of the Buccaneer Field has been compiled (National Marine Fisheries Service, 1977), so only a brief summary is given here.

4.2.1. History

Initial seismic reflection surveys were conducted in Galveston Block 288 from 1953 through 1959. Based upon the results of this survey and regional geological studies, Shell acquired some 43,000 acres at the federal lease sale in February 1960 and proceeded with the drilling of a discovery well. This well reached a total depth of 16,088 feet in November 1960, but mechanical difficulties caused it to be abandoned and no tests were obtained on the potential pay sands.

During 1961 and 1962, additional seismic surveys were performed in Block 288 in order to better assess the size, shape, and complexity of the structural trap. In October 1963, another well was drilled at a location approximately one mile east of the original well. This test well led to a multi-well delineation program. Within a year, 21 additional wells were drilled, 12 of which were cased and completed from 4-pile satellite jackets.

The delineation program indicated that the field reserves were primarily gas, and that those reserves could be most economically developed from two drilling-production platforms. Platform 288-A was installed in September 1964 and 15 wells were drilled from the structure between January and August of 1965. Platform 296-B was placed down in May 1965 and 15 development wells were drilled from it between October 1965 and July 1966.

As the field developed, an onshore gasoline plant was constructed near Freeport, Texas, and the plant was connnected to the field (Platform 288-A) by a 20-inch diameter flowline some 43 miles in length. The pipeline is operated by Blue Dolphin Pipeline Company, a Shell subsidiary. Upon completion of the platform 288-A wells, gas sales commenced on January 1, 1966 at the contract rate of 100 MMCF/day of residue. This was increased in January 1967 to 175 MMCF/day as 296-B began production.

Additional wells were drilled in the field between 1966 and 1971 for the purpose of oil rim development, for geopressured gas and oil, and for untested fault blocks located by seismic reviews. Four wells in those categories have been drilled in Block 289, which was purchased at the May 1968 lease sale. Through June 1971, 81 wells had been drilled in Block 288; of these, 56 were completed and the remainder were plugged. In 1977 there were 34 active wells including 31 gas completions and 3 oil completions. Both production platforms and 6 of the 13 satellite jackets were active. The total fluid stream to the production platforms was approximately 1000 bbl/day from which about 65 MMCF of gas is extracted. The fluid typically contained about 600 bbl produced water and about 400 bbl of crude and condensate. Shell's current lease comprises portions of the Federal Blocks 288, 289, 295, 296 and 322 for a total of 20,070 acres.

Structures that remain in the Buccaneer Field are of five types; production platforms, quarters platforms, satellite well platforms, flare stacks, and pipelines. A total of 18 platforms have been constructed in the field; 2 production platforms, 2 quarters platforms, and 14 satellite platforms.

4.2.2. Production Platforms

The two production platforms in the Buccaneer Field each have two decks approximately 150 ft by 150 ft and supported by piles or legs. A boat landing is located near the water level below the lower deck. The oil and gas lines of the production platforms and from satellite wells enter the structures at the lower deck level.

The separation of oil, gas, condensate, and produced water ("brine") is shown schematically in Figure 1. Produced water flows to "skim tank" vessels, also at atmospheric pressure, located on the lower decks. Most remaining petroleum products are separated there and are put back into the oil-stream flow. Remaining water is discharged overboard. All drains on the production platform, including those from "drip pans", and gutters, flow into the skim tanks. When the study commenced, produced water was discharged from both production platforms. Since November 1978, however, routine discharge has been from Platform 296-B only.

Other structures located on the lower decks of production platforms are seawater pumps. Seawater goes to pressurized lines for fire-fighting systems, and to desalinization plants on the lower decks of the nearby quarters platforms. The pumps are fitted with a back-pressure valve such that excess seawater is discharged when desalinization plants and fire-fighting water lines are at capacity and/or pressure.

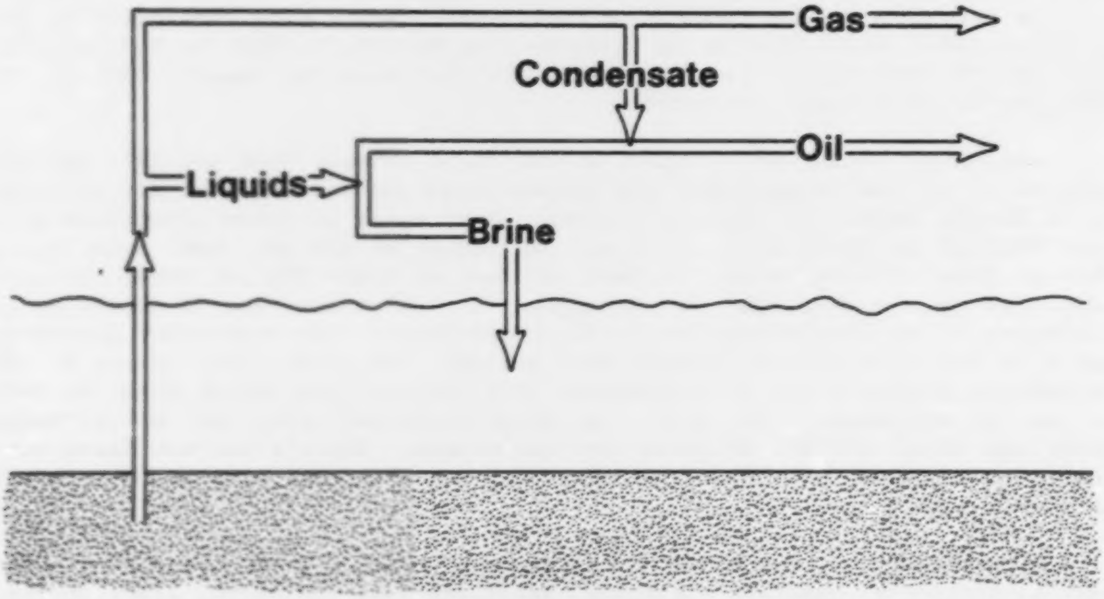

Figure 1. Schematic representation of the separation of oil and gas from brine.

4.2.3. Quarters Platforms

Quarters platforms contain in addition to kitchens, living and recreational quarters, a gas-fired electrical generator, a desalinization plant, and a sewage treatment plant. A helicopter landing pad is located on the upper deck. An upper and lower platform deck are each about 40 ft by 40 ft. All garbage except for food scraps is compacted and transported to shore for disposal; food scraps are collected and dumped overboard. In 1977, about a dozen persons resided in the field, with the work force supplemented as neccesary.

Water needs are normally met by the desalinization plant, although lines are present to take fresh water onto the platform from boats. Raw seawater is pumped continuously through the fresh water condenser, with most of the seawater being discharged overboard.

4.2.4. Flare Stacks

Each of the production platforms has an associated flare stack sited a short distance away from the platform. This is an emergency safety device and no discharges are normally associated with these simple structures. In an emergency, gas is shunted to the flare stacks and ignited to dispose of the discharge.

4.2.5. Sport Fishing and Diving

The Buccaneer Field is a focal point for offshore sport fishing and diving activity in the area. Sport-fishing boats range in size from 16-ft-long boats to large yachts and sailboats. Many of the craft that come to the area are only marginally seaworthy and are in various states of operating efficiency. Fuel is sometimes lost overboard from the vessels; also, bottles and paper containers are frequently thrown overboard from pleasure craft. Raw sewage and food wastes are commonly discharged overboard.

4.2.6. Oil Spills

The Buccaneer Field has a good record in terms of oil spills, with a total of about 250 gallons (6 bbl) reported as spilled. Twenty-one gallons (0.5 bbl) were lost from Platform 296-B on September 28, 1973; 126 gallons (3 bbl) from an unknown source on November 26, 1973; 21 gallons (0.5 bbl) from Platform 296-B on July 21, 1974; 70 gallons (1.7 bbl) from a leak in a line on Platform 296-B on August 6, 1974; and 15 gallons (0.4 bbl) from Platform 288-A on September 30, 1975. No spills were reported during our study.

We have no evidence that oil from the Ixtoc-I blowout or the "Burmah Agate" reached the Buccaneer Field. Most of our sampling had been completed before these incidents.

SECTION 5

EXPERIMENTAL PROCEDURES

Our primary consideration in conducting this study was producing data which were both appropriate and reliable. The program was designed and managed in such a manner that we had adequate flexibility in the sampling protocol to be able to modify it in response to preliminary findings. No arbitrary sampling grid was imposed upon us. Moreover, we were free to use any analytical procedure that we could justify in terms of accuracy, precision, and cost-effectiveness. We were not expected to use any "standard" procedure: consistency with other studies was deemed less important than producing reliable data.

5.1. SAMPLING DESIGN

The types of samples collected, and their locations, are dealt with in detail in the "Results" section, which provides a narrative of the evolution of the project. There were some constraints on the sampling design, but they were not major impediments.

During the first year of the project, facilities were available for the collection of samples only from boats or the production platforms. Sediment samples were, therefore, collected using coring devices, dredges, or grabs. It was not possible to collect sediments from locations close to pipelines because of the risk of rupturing them. Moreover, the boat could not be stationed for sampling close to the platforms.

During subsequent years of the project, divers were available for sample collection. This enabled us to obtain samples from locations very close to and below the platforms. A constraint here was in the number of samples that a team could collect during a desired time period. This problem was exacerbated when synoptic sampling for other studies was performed. On one occasion when sampling scheduled for a single day was extending into a second day, however, we discovered that there was a large day-to-day change in sediment hydrocarbon concentration (see section 6.5.2).

5.2. SAMPLING PROCEDURES

Full details of these procedures were provided in earlier reports (Jackson, 1977, 1979c; Middleditch and West, 1980).

Seawater and discharge samples were collected directly into glass bottles with Teflon-lined screw caps. Sediment samples collected by divers were scooped directly into wide-mouth glass bottles with ground glass stoppers. Other sediment samples were transferred to similar bottles in the field. Some biota samples were collected by hand by divers while others were collected by trawling or by hook-and-line methods. Plankton samples were collected according to MARMAP II protocols

All samples were frozen in the field, whenever practical, to minimize bacterial contamination during transit and storage. Freezers were available both on the boats and on Production Platform 296-B.

5.3. ANALYTICAL PROCEDURES

Full details of these procedures were provided in earlier reports (Jackson, 1977; 1979c; Middleditch and West, 1980).

Particular care was taken to minimize contamination of the samples and to obtain the highest degree of accuracy and precision.

5.3.1. Contamination

Contamination by bacterial metabolites was minimized by freezing the samples as soon as possible after collection and maintaining them in this state until they were analyzed. Some sulfur-bacteria produce hydrocarbons, so this type of contamination would have been particularly serious.

Contamination in the laboratory was minimized by judicious choice of apparatus, solvents, and reagents. Samples were allowed to come into contact with apparatus constructed only of glass, Teflon, and stainless steel. Most plastics contain plasticizers (usually phthalate esters) which interfere with hydrocarbon analyses, so these were not used. All solvents were "distilled-in-glass" grade: less expensive grades contain impurities which interfere with hydrocarbon analyses. Periodic blank analyses were performed, and the validity of analyses performed by gas chromatography (GC) was checked using combined gas chromatography - mass spectrometry (GC-MS).

Some contamination was occasionally encountered, but this was recognized as such and the validity of the data was not compromised. Some batches of cyclohexane were contaminated with bicyclohexyl (Middleditch and West, 1979) which interfered with the determination of n-tridecane. Phthalate esters, one of which had the same retention time as n-pentacosane, were sometimes detected. It was not always possible to determine whether the phthalate esters were contaminants (introduced during sampling or analysis) or whether they were actual components of the samples. We were never able to eliminate chloroform from our blank analyses. However, it did not interfere with our analyses of volatiles.

A related problem is that squalene (a polyunsaturated hydrocarbon common in tissues of marine organisms) interferes with the analysis of n-octacosane if it is not completely removed from the alkane fraction prior to gas chromatography.

5.3.2. Accuracy and Precision

Complete extraction of hydrocarbons is required to obtain an accurate estimate of their concentration. If extraction is incomplete but reproducible, accuracy will suffer but precision will be maintained. It is impossible to determine whether complete extraction is being obtained from a "real" sample. Our procedure achieve the recovery of more than 95% of added hydrocarbon, but this does not prove that a similar proportion of endogenous hydrocarbon is being extracted. If the residue of a sample is further extracted after our routine extraction procedure, no more than 5% of additional hydrocarbon can be obtained, even using exhaustive methods. Again, this does not prove that at least 95% of the total hydrocarbon content is recovered: some endogenous hydrocarbon may not be amenable to extraction.

To optimize the recovery of hydrocarbons from tissue and sediment samples, they were homogenized by a combination of mechanical and ultrasonic action and then saponified prior to solvent extraction. The objective was to break up the sample as much as possible so that a large surface area could be exposed to solvents. Thus, the saponfication step was employed to degrade cell membranes as much as to hydrolyze polar lipids.

The small quantities of hydrocarbons present in many of the seawater samples could have been lost by adsorption onto glass surfaces if precautions had not been taken to minimize this effect. Seawater samples were collected directly into 1-liter glass bottles. Only about 800 ml was collected in each bottle so that there was room for expansion during freezing. This also left sufficient room in the same bottles for addition of the solvent used for extraction. Solvent was tumbled with the sample in these bottles for 24 hours to extract hydrocarbons both from the water and from the glass itself.

Even if complete extraction is obtained, the accuracy of the method can suffer if there are losses of hydrocarbons before the final step of the analysis. If these losses vary from sample to sample, precision will also be imparied. A simple method of avoiding this problem involves the use of isotope-labeled internal standards, a method that has been used in biomedical research for more than a decade. Addition to the sample of an isotope-labeled analog of the substance of interest prior to extraction will compensate both for losses of the material after extraction and for injection errors in gas chromatography.

We used isotope-labeled internal standards for all of the analyses. In most instances a mass spectrometer is required as the gas chromatographic detector to differentiate between the labeled and unlabeled species (Sweeley *et al.*, 1966). For n-alkanes, however, each perdeuteriated compound is completely separated from the corresponding unlabeled n-alkane. Thus, no mass spectrometer is required to differentiate these pairs of compounds, even when conventional packed gas chromatographic columns are employed (Middleditch and Basile, 1976).

The various compounds employed for hydrocarbon analysis were n-[$^2H_{66}$]dotriacontane, [$^2H_{10}$]pyrene, [$^2H_{12}$]benzanthracene, [$^2H_{10}$]-1-methylnaphthalene, [$^2H_{10}$]-2-methylnaphthalene, and [$^2H_{12}$]benzo[*a*]-pyrene. An appropriate quantity of the deuteriated hydrocarbons was added to the sample before analysis. For example, 2 µl of a 0.1% solution added to 1 l of seawater afforded a concentration of 2 ppb.

We used sulfur enriched in sulfur-34 as the internal standard for the analysis of elemental sulfur (Middleditch and Basile, 1979).

In summary, we are no more certain of the accuracy of our analytical procedures than anyone can be, but we were using state-of-the-art methods to maintain optimum accuracy and precision. If the precision of our analytical techniques was inadequate we would not, for example, have been able to discern concentration gradients in the vicinity of the production platforms (see section 6.5.2). Our integrated analytical procedure is illustrated for sediment samples in Figure 2.

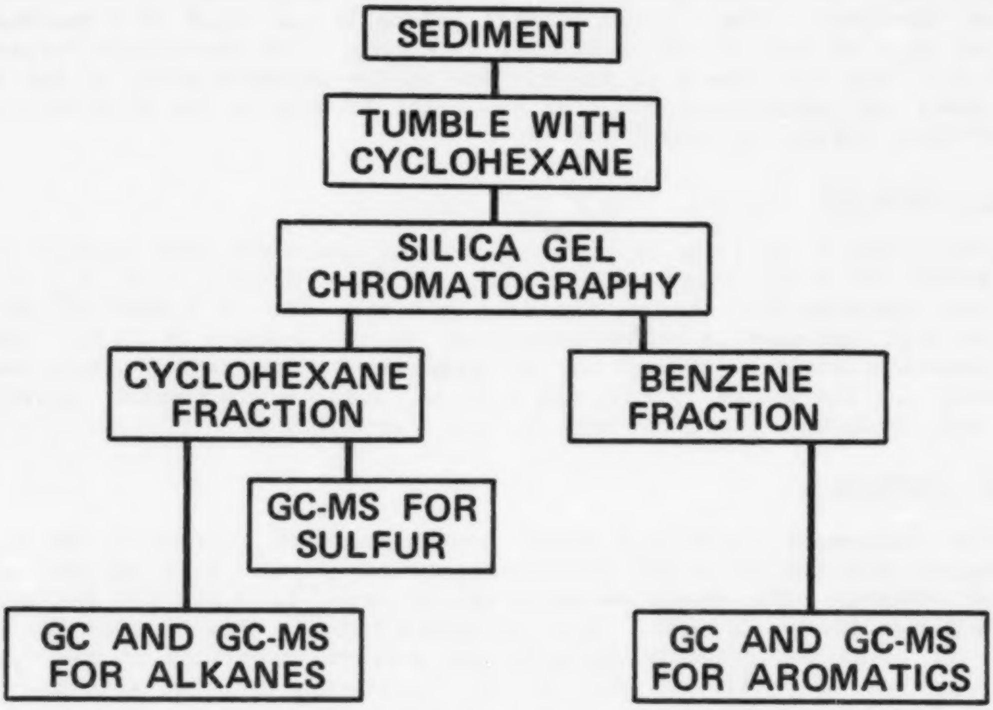
SEDIMENT
TUMBLE WITH CYCLOHEXANE
SILICA GEL CHROMATOGRAPHY
CYCLOHEXANE FRACTION
BENZENE FRACTION
GC-MS FOR SULFUR
GC AND GC-MS FOR ALKANES
GC AND GC-MS FOR AROMATICS

Figure 2. Integrated analytical procedure for alkanes, aromatic hydrocarbons, and sulfur, illustrated for sediments.

SECTION 6

RESULTS

6.1. OIL AND CONDENSATE

Oil and condensate were examined, not because they are discharged from the platforms but because a knowledge of their composition was an aid to interpreting other observations. Figure 1 shows the product flow on the production platforms. The oil was sampled before it was mixed with condensate. A third type of sample (not indicated in Figure 1) is designated "separator tank oil." Some oil floats to the surface of the produced water in the final skim tank; the composition of this is similar to that of the produced water, and provides additional useful data.

6.1.1. Crude Oil

The alkane composition of the crude oil is consistent with reports on the composition of other crude oils (Smith, 1968). Alkanes from C_{12} to C_{36} comprise approximately 18% of the oil, and they show a decreasing concentration with increase in chain length and an OEP average of 1.02. The n-heptadecane/pristane ratio and the n-octadecane/phytane ratio, often used as indicator for the source of oil, are 0.90 and 2.44, respectively. Crude oils from both production platforms have similar compositions.

6.1.2. Condensate

The condensate contains a lower concentration of alkanes in the C_{12} to C_{36} region than the crude oil (approximately 14%), and larger amounts of the lighter alkanes. The n-heptadecane/pristane ratio is 1.30, and the n-octadecane/phytane ratio is 3.33. The difference between these ratios and those found for crude oil probably reflects the greater volatility of the C_{17} and C_{18} n-alkanes, compared with that of the C_{19} and C_{20} branched alkanes. Condensate from both platforms was similar in composition.

6.1.3. Separator Tank Oil

The major components of the separator tank oil were, again, the n-alkanes. Their relative concentrations also decreased with chain length, and the heaviest alkanes seen were usually around C_{30}. A typical analysis of the non-volatile components is given in Table 2. The n-heptadecane/pristane ratio is 1.70, and the n-octadecane/phytane ratio is 6.76.

TABLE 2. SEPARATOR TANK OIL: JUNE 24, 1979

Peak	I^a	Component	ppm
1	1100	n-Undecane	5,840
2	1105	C_4-Benzene	57
3	1133	C_4-Benzene	216
4	1156	Naphthalene	537
5	1200	n-Dodecane + C_5-Benzene	8,790
6	1214	Branched tridecane	2,400
7	1267	2-Methylnaphthalene	519
8	1277	Branched tetradecane	3,250
9	1281	1-Methylnaphthalene	486
10	1300	n-Tridecane	10,890
11	1317	C_7-Benzene	40
12	1347	Acenaphthene or Biphenyl	162
13	1363	C_2-Naphthalene	94
14	1374	C_2-Naphthalene	203
15	1287	C_2-Naphthalene	400
16	1390	C_2-Naphthalene	61
17	1400	n-Tetradecane	13,850
18	1405	C_2-Naphthalene	193
19	1417	C_2-Naphthalene	81
20	1441	?	45
21	1450	Methylbiphenyl	245
22	1463	Branched pentadecane	6,220
23	1469	?	41
24	1492	C_3-Naphthalene	114
25	1500	n-Pentadecane	13,750
26	1513	C_3-Naphthalene	164
27	1530	C_3-Naphthalene	234
28	1543	C_2-Biphenyl	44
29	1550	C_3-Naphthalene	178
30	1557	C_2-Biphenyl	1,970
31	1563	Branched alkane	75
32	1565	?	41
33	1582	?	41
34	1600	n-Hexadecane	11,690
35	1618	C_4-Naphthalene	45
36	1638	C_4-Naphthalene	57
37	1644	?	55
38	1651	C_4-Naphthalene + branched alkane	3,310
39	1671	?	61
40	1694	C_4-Naphthalene	111
41	1700	n-Heptadecane	11,260
42	1709	Pristane	6,630
43	1763	?	1,090
44	1800	n-octadecane	8,720

(continued)

TABLE 2 (continued)

45	1811	Phytane	1,290
46	1900	n-Nonadecane	6,500
47	2000	n-Eicosane	3,850
48	2100	n-Heneicosane	2,850
49	2200	n-Docosane	2,700
50	2300	n-Tricosane	2,420

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[a] I = Retention index.

The n-heptadecane/pristane and n-octadecane/phytane ratios are frequently used to characterize spilled oil. The values reported here for the crude oil would be appropriate for this purpose if a spill of crude oil were to occur. However, the different ratios for condensate or separator tank oil should be used if these materials were to be spilled. Moreover, if there were to be a spill from a leaking pipeline, a different ratio might be anticipated. In such a case, it would be prudent to obtain a sample of the oil at its source for comparison with environmental samples.

6.2. PRODUCED WATER

Many analyses of produced water were performed during our study. During the early years of the survey, we used alkanes as "markers" for tracing the distribution of oil field contaminants throughout the area, so we concentrated on the alkane content of the produced water. We later added methylnaphthalenes and benzo[a]pyrene as markers for the light and heavy aromatic hydrocarbons, respectively. We also determined the concentrations of elemental sulfur. Several detailed analyses were carried out to obtain a more complete inventory of the composition of the produced water. Finally, the biocide content of these discharges was investigated.

6.2.1. Heavy Alkanes

The protocol used for this analysis provided quantitative data for alkanes greater in molecular weight than dodecane. n-Alkanes with chain lengths to C_{38} were found, with odd-even preference values of around unity. The n-heptadecane/pristane ratios for the discharged brine range from 0.89 to 1.25 (mean, 1.05), while value for the n-octadecane/phytane ratios range from 1.0 to 5.26 (mean, 2.44). These ratios are closer to those for the crude oil than to those for the condensate and separator tank water.

Most of the produced water samples exhibited concentration maxima below n-C_{23}. It is possible that differences in maxima are due to varying degrees of evaporation of the lighter alkanes. Thus, a sample collected at 20°C from Platform 296-B on March 8, 1977 exhibited a concentration maximum below C_{11} and an alkane concentration of 6.2 ppm (Figure 3), whereas a sample collected at 28°C on the same day from Platform 288-A exhibited a concentration maximum at C_{17} and an alkane concentration of 570 ppb (Figure 4).

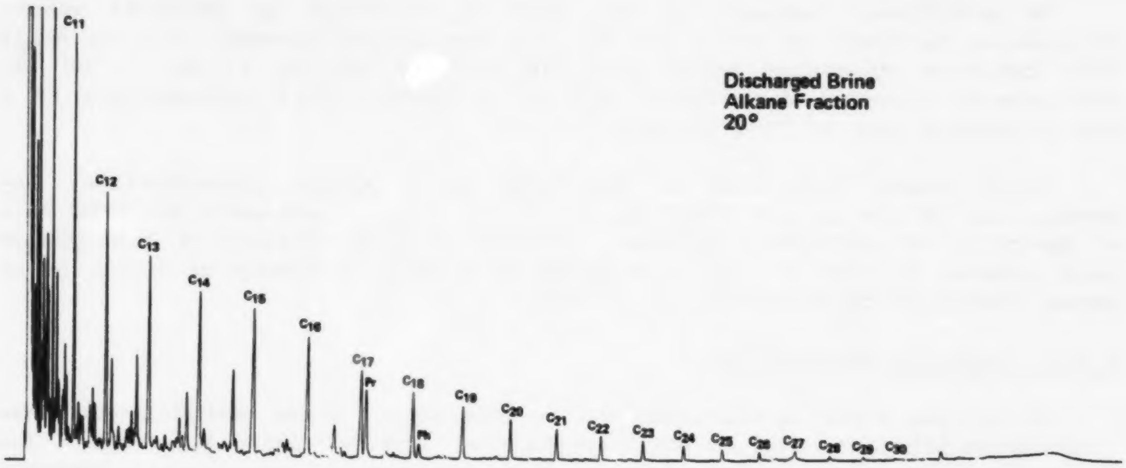

Figure 3. Gas chromatogram for alkane fraction of produced water discharged from Platform 296-B on March 8, 1977 at 20°C.

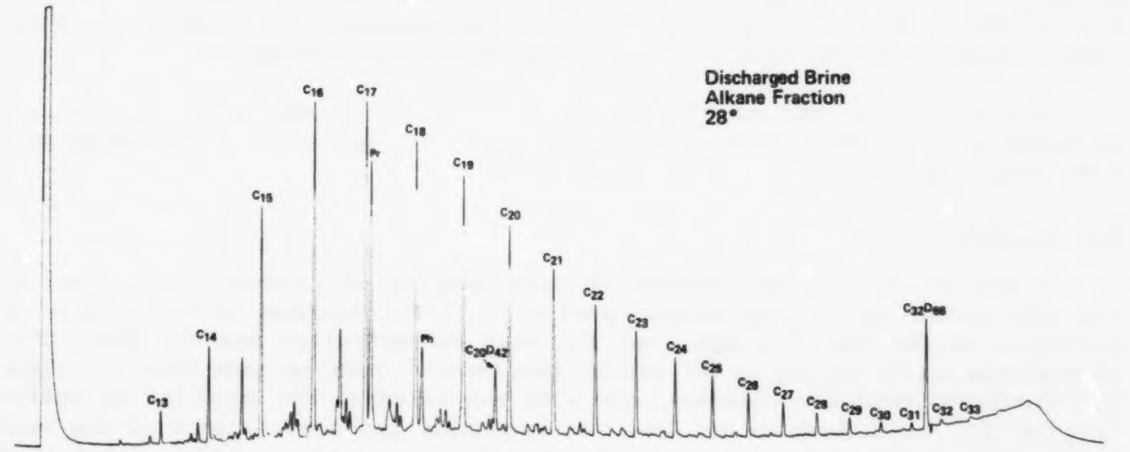

Figure 4. Gas chromatogram for alkane fraction of produced water discharged from Platform 288-A on March 8, 1977 at 28°C.

Moreover, the concentration of the alkanes in the produced water varies with time. Ten samples collected over a 30-hour period on September 2-3, 1978 had a mean alkane concentration of 2.98 ppm, but concentrations in individual samples ranged from 0.9 to 4.8 ppm.

An additional variable is the rate of discharge of produced water. Information provided by Shell Oil Co. for the period November 1973 to April 1978 indicates discharge rates from 118 to 2000 bbl/day (1 bbl = 159 l). Measurements reported for August 1979 by Gallaway (1980) corresponded to a mean discharge rate of 1000 bbl/day.

Given these variations in discharge rate, alkane concentration, and composition of the alkane fraction, it is not easy to estimate the mean rate of discharge of individual alkanes. However, a concentration of 3.37 ppm of total alkanes in 1000 bbl/day corresponds to a daily discharge of 560 g, or an annual discharge of approximately 200 kg.

6.2.2. Aromatic Hydrocarbons

Particular emphasis was given during this study to the methylnaphthalenes (1-methylnaphthalene and 2-methylnaphthalene) and to benzo[a]pyrene. The former compounds were chosen as being characteristic of the lighter aromatic hydrocarbons (which are relatively soluble and exhibit toxicity toward many marine organisms), while benzo[a]pyrene is typical of the less soluble polycyclic aromatic hydrocarbons (some of which are carcinogens). Concentrations for the individual methylnaphthalenes were determined. The ratio of 2-methyl isomer to 1-methyl isomer was approximately 5:4 and relatively constant. Only the total methylnaphthalene concentrations are discussed here.

Methylnaphthalenes were detected in most samples of produced water. Their mean concentration was 43 ppb, while concentrations up to 170 ppb were encountered. This corresponds to a mean discharge rate of about 7.1 g/day or 2.6 kg/year. This is much less than for the alkanes. In determining their significance, however, relative toxicities should be considered.

Concentrations of benzo[a]pyrene as high as 5 ppb were occasionally encountered. The mean concentration was only 1.2 ppb which corresponds to a mean discharge rate of 0.2 g/day or 72 g/year.

6.2.3. Sulfur

Elemental sulfur was visible in most samples of produced water, and it was determined by a gravimetric procedure. The maximum concentration of elemental sulfur was 1200 ppm, and the mean concentration was 460 ppm. This corresponds to 73 kg/day or 27 metric tons/year. This is more than 100 times the discharge rate for alkanes. As with the alkanes, the toxicity of sulfur is generally considered to be low. In assessing the significance of the very large amounts of sulfur being discharged, however, its potential value as a nutrient should also be considered.

The concentration of sulfur in the produced water changes throughout the day and is unrelated to the alkane concentration.

6.2.4. Biocides

Biocides used in the Buccaneer Field at the start of the study were K-31 (pentanedialdehyde) and KC-14 (alkyldimethyl benzyl chloride), both manufactured by Champion Chemical Company. In addition, a surfactant (Surfatron DQ44) was also employed. The weekly alternation in application of the two biocides was only partially successful in reducing the numbers of Desulfovibrio so, in April 1978, Shell switched to the acrolein biocide Magnacide B (Magna Corporation).

Magnacide B is a formulation of acrolein (2-propenal) of approximately 90-94% purity, depending on the source. The acrolein is not manufactured by Magna but is distributed and applied by this EPA licensed applicator. Acrolein is a highly volatile, toxic, and reactive substance. Residual acrolein in produced water is scavenged by treatment with sodium bisulfite (Magnatreat OS-L) prior to discharge.

The orginal biocides and surfactant were found to be contaminated with alkanes: K-31, 1.89 ppm; KC-14, 1.60 ppm; DQ44, 3.26 ppm. They contributed a negligible amount to the total alkane content of the produced water discharge. A spectrophotometric assay for these substances was being developed when their use was discontinued.

The determination of acrolein in aqueous solution is a difficult analytical problem. It is not amenable to the regular purge-and-trap technique commonly used for the determination of low-molecular weight substances by GC-MS. The preliminary "priority pollutant" protocol for acrolein called for direct aqueous injection into a water-compatible GC column. We were able to obtain greater sensitivity with a purge-and-trap method carried out at elevated temperature - this is also the most recently recommended "priority pollutant" method for acrolein. Even so, the detection limit is only 100 ppb (compared with 10 ppb for most other organic priority pollutants). We were unable to detect acrolein in any produced water samples by this technique. This problem may have been exacerbated by the instability of acrolein in aqueous solution. If some acrolein had been present in these samples at the time of collection, it might have been dissipated by the time that they reached the laboratory.

Information provided by Shell indicated that residual amounts of acrolein in the range 1-3 ppm were measured in produced water immediately after the installation of the injection system, when sufficient time had probably not elapsed for equilibration of acrolein usage concentration, bacterial counts, and scavenger usage concentrations. Once this had been done no residual was detected until a pump failed and was replaced, when acrolein levels of 2 ppm were reported. After three days, residual acrolein was again below detection limits. The detection limit of the assay procedure employed was apparently 1 ppm.

Given the high reactivity and low half-life of acrolein in the water disposal system and more than adequate means of neutralizing any possible residual it is strongly suspected that little, if any, is even reaching the

TABLE 3. VOLATILES IN PRODUCED WATER DISCHARGE: JANUARY 14, 1979

Peak	Component	ppb
1	2-Methylbutane	960
2	Chloroform (artifact)	100
3	2-Butanone	300
4	n-Pentane	720
5	Cyclohexane	520
6	?	660
7	Methylcyclopentane	460
8	3-Methylpentane	80
9	?	80
10	Benzene	6100
11	?	60
12	2-Pentanone	160
13	Heptane	80
14	n-Hexane	460
15	1,3-Dimethylcyclopentane	240
16	Methylcyclohexane	1080
17	Octadiene	40
18	Heptane	80
19	Heptane	100
20	Heptane	80
21	Octene	380
22	3-Methylhexane	200
23	Heptane	240
24	Octane	80
25	Toluene	5460
26	2,2-Dimethyl-3-hexene	160
27	Dimethylcyclohexane	120
28	Octane	40
29	Dimethylcyclohexane	80
30	Trimethylcyclohexane	80
31	Ethylbenzene	1200

ocean. Even if trace amounts should enter the environment they would not be expected to be persistent, but easily and quickly dispersed and inactivated.

6.2.5. Other Contaminants

One of the tasks that we undertook during this study was to identify and quantitate as many as possible of the components in the produced water discharge.

TABLE 4. EXTRACTABLES IN PRODUCED WATER: JUNE 1979

Peak	I^a	Component	ppb
1	1018	C_3-Benzene	12.5
2	1039	C_3-Benzene	11.7
3	1062	C_4-Benzene	1.7
4	1065	C_4-Benzene	0.4
5	1068	C_4-Benzene	1.8
6	1073	C_4-Benzene	1.5
7	1084	C_4-Benzene	3.6
8	1088	C_4-Benzene	2.4
9	1092	C_4-Benzene	2.4
10	1102	C_4-Benzene	1.7
11	1113	C_5-Benzene	1.8
12	1118	C_4-Benzene	3.2
13	1133	C_5-Benzene + $C_{5:1}$-Benzene	0.4
14	1130	C_4-Benzene	5.2
15	1148	C_5-Benzene	0.4
16	1156	Naphthalene	11.1
17	1158	$C_{5:1}$-Benzene	0.5
18	1159	C_5-Benzene	0.6
19	1160	C_5-Benzene	0.8
20	1162	C_6-Benzene + $C_{6:1}$-Benzene	0.7
21	1172	C_6-Benzene	1.3
22	1186	C_6Benzene	0.3
23	1193	?	0.5
24	1243	C_6-Benzene	0.4
25	1249	C_6-Benzene	0.5
26	1255	?	0.7
27	1281	1-Methylnaphthalene	7.2
28	1307	?	0.5
29	1320	C_7-Benzene	0.9
30	1338	?	0.3
31	1348	Biphenyl or Acenaphthene	2.8
32	1364	C_2-Naphthalene	1.0
33	1376	C_2-Naphthalene	1.8
34	1390	C_2-Naphthalene	4.0
35	1393	C_2-Naphthalene	1.0
36	1398	C_8-Benzene	0.5
37	1400	n-Tetradecane	22.5
38	1403	C_2-Naphthalene	1.7
39	1418	C_2-Naphthalene	0.9
40	1424	C_8-Benzene	0.4
41	1442	C_8-Benzene	0.7
42	1452	Methylbiphenyl	2.3
43	1458	?	0.5
44	1476	C_3-Naphthalene	0.6

(continued)

TABLE 4 (continued)

45	1488	$C_{8:1}$-Benzene	0.5
46	1494	C_2-Biphenyl + C_3-Naphthalene	0.6
47	1500	C_3-Naphthalene + n-Pentadecane	b
48	1516	C_3-Naphthalene	1.1
49	1526	?	0.4
50	1532	C_3-Naphthalene	1.2
51	1535	C_9-Benzene	1.0
52	1542	C_9-Benzene	0.5
53	1552	C_3-Naphthalene	1.4
54	1558	C_2-Biphenyl	0.4
55	1584	C_{10}-Benzene	0.5
56	1600	n-Hexadecane	35.7
57	1641	C_{10}-Benzene + C_4-Naphthalene	0.5
58	1662	C_{10}-Benzene + C_4-Naphthalene	0.5
59	1697	C_4-Naphthalene + C_5-Naphthalene	0.4
60	1700	n-Heptadecane	29.6
61	1764	C_{11}-Benzene	0.3
62	1800	n-Octadecane	31.0
63	1868	?	0.5
64	1900	n-Nonadecane	35.4
65	2000	n-Eicosane	32.7
66	2100	n-Heneicosane	50.0
67	2200	n-Docosane	77.4
68	2300	n-Tricosane	197.1
69	2400	n-Tetracosane	248.0
70	2500	n-Pentacosane	208.6
71	2600	n-Hexacosane	170.7
72	2700	n-Heptacosane	128.5
73	2800	n-Octacosane	103.2
74	2900	n-Nonacosane	105.1

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[a] I = Retention index, [b] a C_3-naphthalene is obscured by n-pentadecane

We were not satisfied with the degree of accuracy that could be attained using existing procedures for the analysis of volatiles. Indeed, as of December 1979 the EPA had not evaluated the accuracy and precision of the "priority pollutant" method for volatiles. Accordingly, we developed a procedure employing [$^2H_6$]benzene as internal standard. Results of a typical analysis are given in Table 3. Most of the volatile components were expected petroleum hydrocarbons. Chloroform was an artifact which appeared in blank analyses and could not be eliminated. The 2-butanone and 2-pentanone were probably from solvent employed by painters on the platforms. In July 1979 a 55-gallon drum of "methyl ethyl ketone" (2-butanone) was in use on Platform 296-B for this purpose. 2-Pentanone is a known contaminant of technical grade methyl ethyl ketone. Runoff from the platform is chanelled to the skim tanks, so this is the probable source of these compounds.

Responsibility for the analysis of volatile components of the discharges passed to Dr. James Brooks of Texas A&M University in August 1979: his data are presented in an accompanying report.

A typical analysis of the produced water extractables is given in Table 4. All of these compounds are expected petroleum constituents.

The total number of components identified in produced water is:

Volatiles (Table 3)	30
Extractables (Table 4)	84
Other n-alkanes (C_{30} to C_{38})	9
Benzo[a]pyrene	1
Sulfur	1
TOTAL	125

Many additional compounds could be found if specific analyses were performed, as for benzo[a]pyrene.

6.2.6. Priority Pollutants

Attention is given here to the organic priority pollutants because they are featured in the new Ocean Discharge Criteria (Federal Register, February 12, 1980). At the detection limits of the priority pollutant protocol (generally, 10 ppb), only the following would be reported:

Acenaphthylene
Benzene
Ethylbenzene
Naphthalene
Toluene

Acrolein and benzo[a]pyrene are discussed above. The recently issued Consolidated Permit Regulations (Federal Register, May 19, 1980) list 79 substances in addition to the priority pollutants. Of those which are organic compounds, we detected only cyclohexane. Xylenes were almost certainly present but were too volatile for analysis as extractables and insufficiently volatile for detection by the protocol that we employed for volatiles. Isoprene may also have been present, but it is too volatile for analysis by the standard purge-and-trap procedure.

6.3. OTHER PLATFORM DISCHARGES

The rate of treated sewage discharge from Platform 296B is about 30 liters per hour, but it flows on an intermittent basis. Alkane concentrations in sewage were as high as 800 ppb but the alkane/isprenoid ratios were not typical of petroleum, and C_{17}, C_{18}, and C_{20} alkanes usually predominated. Also, most samples showed a strong odd-carbon preference, indicating biogenic alkanes. It is likely that alkanes in sewage represent biogenic input from bacteria or feces, for example (Figure 5).

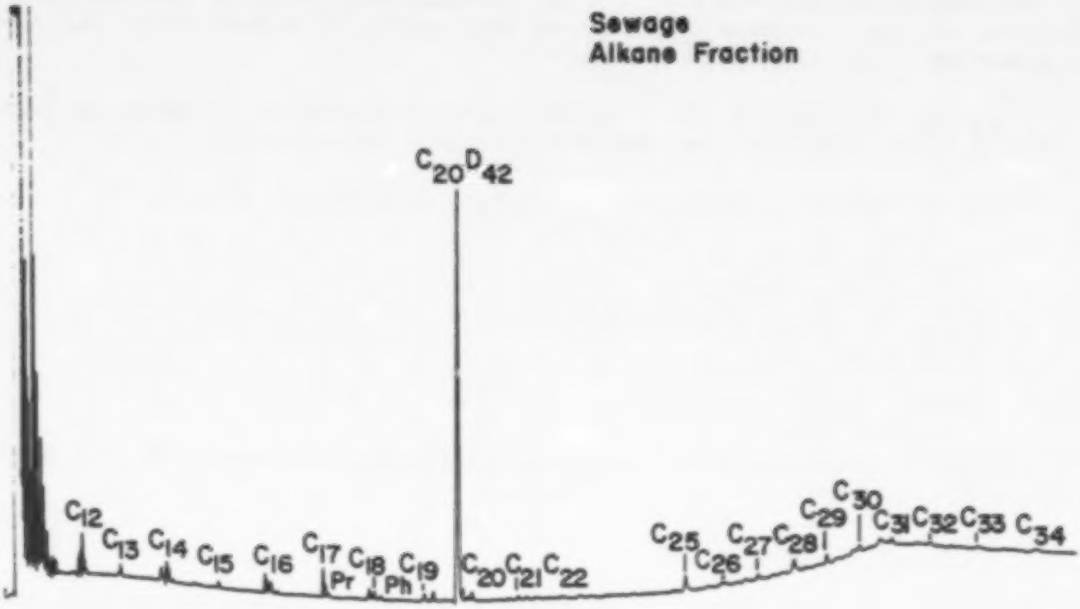

Figure 5. Gas chromatogram for alkane fraction of sewage discharged from Platform 296B (August 6, 1978).

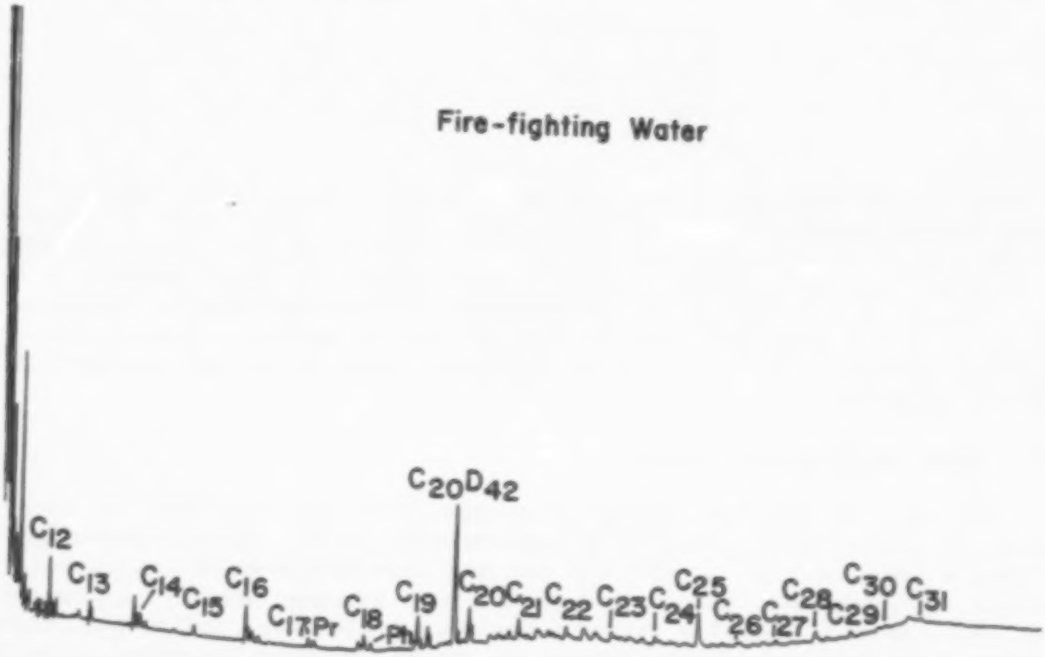

Figure 6. Gas chromatogram for alkane fraction of fire-fighting water discharged from Platform 296B (February 18, 1979).

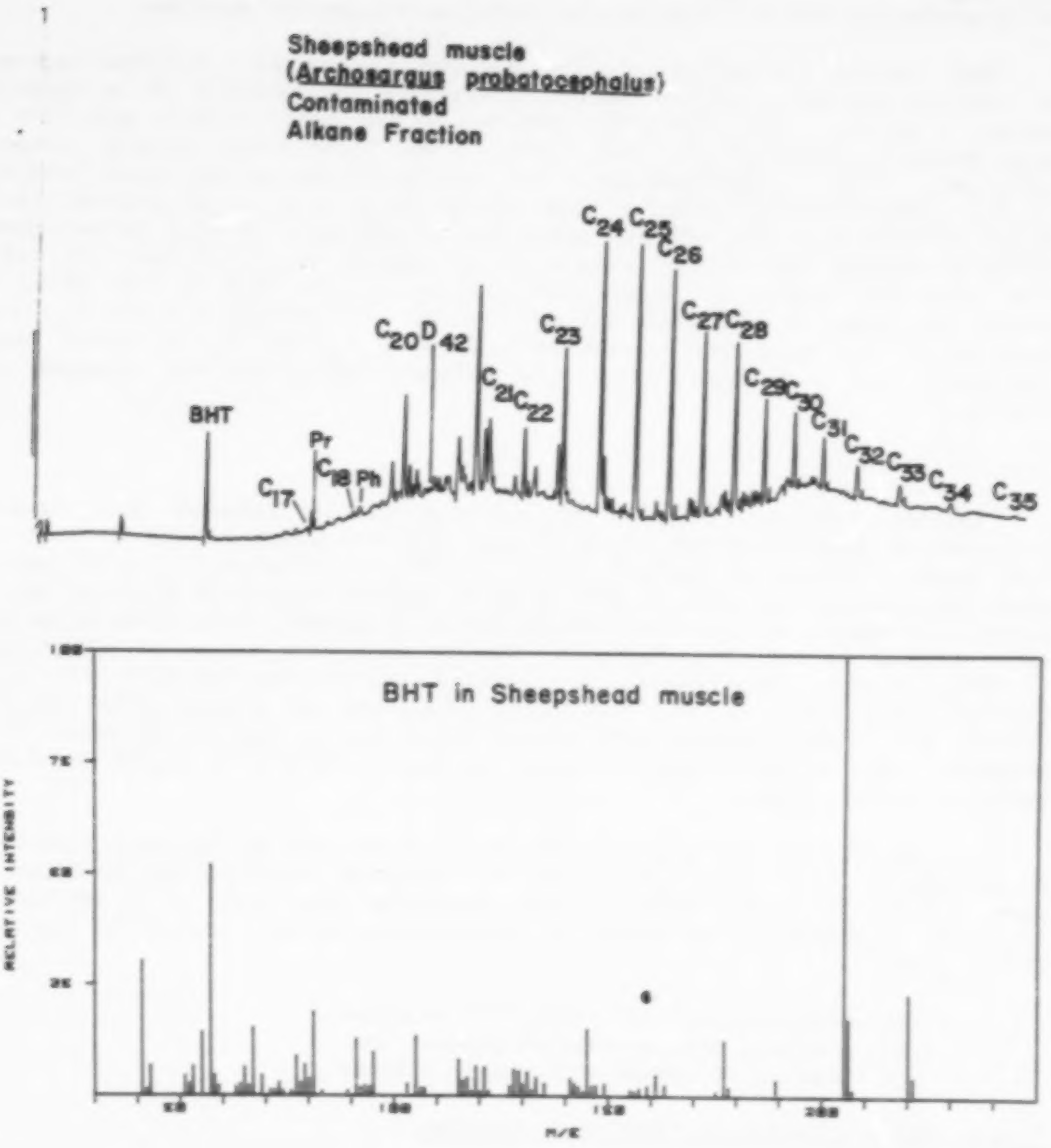

Figure 7. Gas chromatogram of alkane fraction of sheepshead (*A. probatocephalus*) muscle containing BHT (upper), and mass spectrum of this component (lower) collected August 24, 1978: sample SH 18M.

Overflow from the fire-fighting system had an alkane content which was generally in the range of 1-5 ppb. In addition to the petroleum alkanes, some samples contained a group of unresolved hydrocarbons in the region C_{20} to C_{30} (as seen in Figure 6). These compounds were particularly notable (44 ppb) in one sample. It is possible that they derived from a rubber hose. One sample of fire-fighting water contained the bacterial metabolite squalene.

Food scraps are dumped into the sea from the quarters platform adjacent to Platform 296-B. Platform personnel estimate the quantity to be approximately 1 kg/day. Fish have been observed eating these scraps, and some of this material (particularly corn kernels) was found among stomach contents (Gallaway, 1980). Interestingly, the food preservative butylated hydroxytoluene (BHT) was identified in the alkane fraction of a sheepshead muscle sample (Figure 7). The BHT was particularly prominent in this chromatogram, probably because the alkane content of the sample was relatively low and a high gain was needed to detect the alkanes. With such a high gain, an unresolved "hump" of petroleum hydrocarbons was seen between C_{17} and C_{25}. [The baseline of the chromatogram rose again between C_{25} and C_{31} as column bleed increased, and then fell after the column temperature had reached its maximum.]

6.4. SEAWATER

Initial studies (1976-77) of hydrocarbons in seawater used samples collected at many locations, both adjacent to the platforms and up to 10 km from them. Occasional surface seawater samples contained up to 30 ppb of petroleum alkanes and some bottom seawater samples contained up to 25 ppb of biogenic alkanes. No concentration gradients of alkanes were found in surface water samples around the platforms. During the period August 31 - September 1, 1976, however, relatively high concentrations of alkanes were seen downcurrent (southwest) of the production platforms in bottom water samples (Figure 8). These alkanes were in the range C_{25} to C_{35} and appeared to be biogenic, with a distribution similar to those produced by sulfur-utilizing bacteria (Davis, 1968).

The vessel used for sampling during the first year of the study could not be maneuvered close to the platforms, so subsequent sampling was by divers or from a small inflatable boat. Three approaches were used in an attempt to delineate concentration gradients of contaminants in the vicinity of the discharge pipes:

(1) three-dimensional "bullseye" sampling,
(2) sampling from dye-marked plumes, and
(3) tagging effluents with single alkanes.

7.4.1. Three-dimensional "Bullseye" Sampling

Samples were collected from the air/sea interface, at depths of 3, 5, and 8 m from the surface, and at the sediment/water interface. At each depth, a sample was taken directly below the discharge pipe, and an additonal 4-12 samples were taken on transects extending N, S, E, and W of these points. This sampling was repeated during the four seasons of 1978-79. Measurable

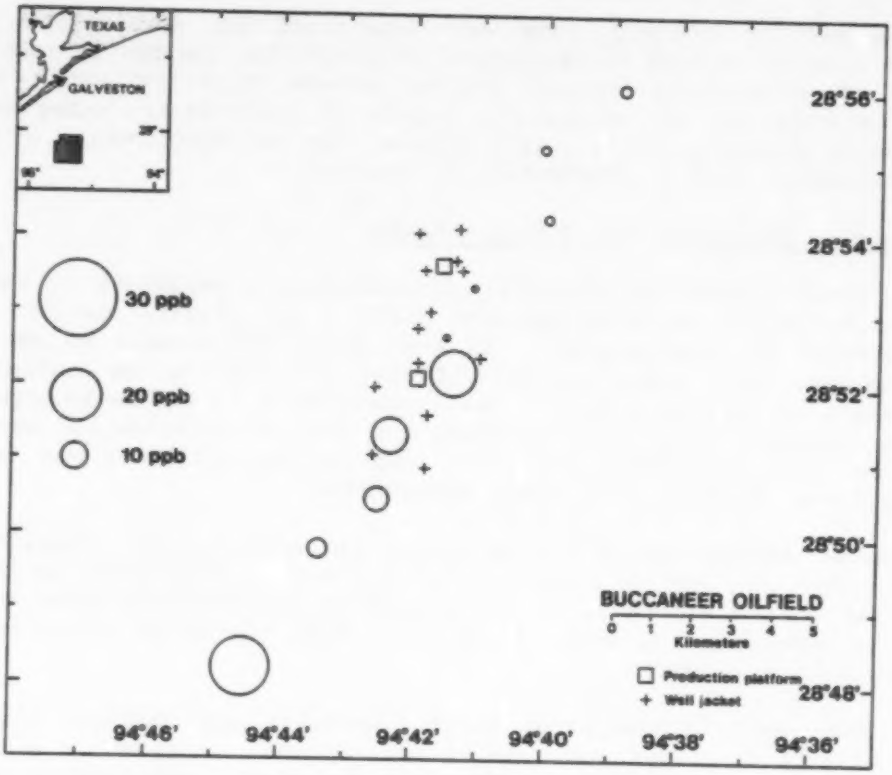
TEXAS
GALVESTON
29°
95°
94°
28°56'
28°54'
28°52'
28°50'
28°48'
30 ppb
20 ppb
10 ppb
BUCCANEER OILFIELD
0 1 2 3 4 5
Kilometers
Production platform
Well jacket
94°46'
94°44'
94°42'
94°40'
94°38'
94°36'

Figure 8. Distribution of biogenic alkanes in bottom water samples during August 31 - September 1, 1976.

amounts of petroleum alkanes were usually found directly below the discharge pipe at the air/sea interface and at nearby sampling sites. However, there were no clearly defined concentration gradients. Moreover, the distribution of contaminants was not related to wind or current strength or direction.

6.4.2. Sampling from Dye-marked Plumes

Other investigators used Rhodamine WT dye to investigate the distribution of effluents from the platforms (Armstrong, 1979; Workman and Jones, 1979). Under calm conditons the dye-marked plumes were relatively static and dye penetrated to depths as great as 10 m from the surface. On other occasions, currents swept the dye-marked plumes away from the platforms.

We conducted a similar experiment at a time when the current was flowing at about 3 knots. Rhodamine WT dye was poured into the sea during two consecutive produced water discharge cycles. Care was taken to ensure that the dye and discharge entered the sea at the same point simultaneously. Each of the two resulting dye patches was carried away from the platform, and they were sampled from a rubber boat.

Alkane and dye concentrations were determined for each sample. While there were clearly defined concentration gradients for the dye in each patch, there was no correlation between dye and alkane concentrations. We were unable to account for any significant source of hydrocarbons other than the produced water discharge, so it was concluded that the distribution of the dye did not correspond to the distribution of alkanes.

6.4.3. Tagging Effluents with Single Alkanes

In a final attempt at identifying concentration gradients in the water column, we decided to use a marker with chemical and physical properties more closely similar to hydrocarbons. It was deemed undesirable to use hydrocarbons labeled with radioisotopes if samples were to be collected by divers. Also, we were reluctant to use large amounts of stable isotopes in an area under intensive scientific scrutiny for fear of invalidating any future study. The only reasonable method of tagging the effluents was to add a relatively large quantity of a single hydrocarbon.

It seemed appropriate to use an alkane for this purpose, since they are non-toxic, odorless, and colorless. The C_{20} alkane n-eicosane was selected since it was in the mid-range of the alkanes in the produced water and since (unlike the odd-carbon alkanes) it is not among the major biogenic hydrocarbons in most organisms.

The total daily discharge of heavy alkanes is approximately 560 g. n-Eicosane usually comprises about 5% of this amount, or about 30 g per day. The produced water discharge generally flows for about three minutes at a time every six minutes. Thus, each three-minute discharge contains about 0.125 g of n-eicosane. We decided to add 1 kg of n-eicosane to the discharge on one occasion during each of six consecutive days to determine its distribution in the environment. This quantity was considerably greater than either the amount in a single discharge or a single day. Also, the amount of n-eicosane used during the six-day period was more than 30 times the amount in the produced water discharge during that time period.

We purchased 6 kg of n-eicosane from a reputable supplier and analyzed it prior to use. It was found to contain only 27% of n-eicosane along with other n-alkanes. It was apparently paraffin wax and was unsuitable for our experiment. In the brief time period (less than 24 hours) before the vessel sailed we were not able to obtain a further supply of 6 kg of n-eicosane, but we were able to purchase 3 kg of n-octadecane, 2 kg of n-eicosane, and 1.5 kg of n-docosane. We modified our protocol to use 0.75 kg of n-docosane on each of the first two days, 1 kg of n-eicosane on each of the next two days, and 1.5 kg of n-octadecane on each of the last two days.

Samples of seawater from the air/sea interface collected below the discharge pipe immediately after each release of hydrocarbon contained the appropriate hydrocarbon in concentrations higher than would be expected if the sample contained only the hydrocarbons from the produced water discharge. No

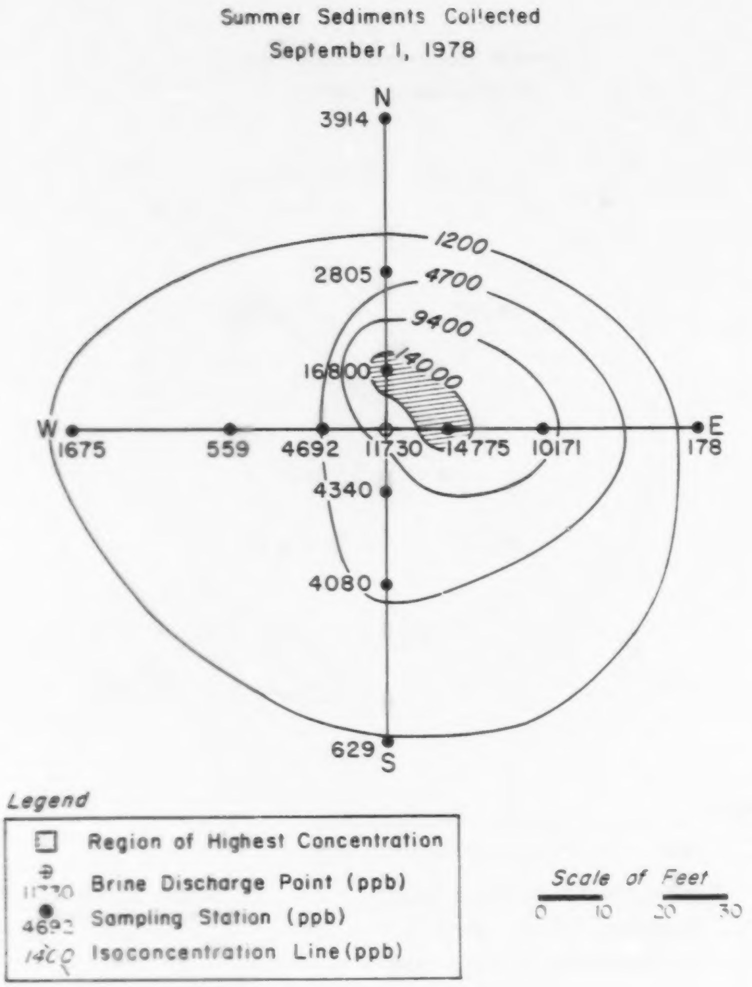
Summer Sediments Collected
September 1, 1978
N
3914
1200
2805
4700
9400
16800
14000
W
1675
559
4692
11730
14775
10171
E
178
4340
4080
629
S
Legend
Region of Highest Concentration
11730 Brine Discharge Point (ppb)
4692 Sampling Station (ppb)
1400 Isoconcentration Line (ppb)
Scale of Feet
0 10 20 30

Figure 9. Distribution of alkanes in surficial sediments on September 1, 1978.

excess of the added hydrocarbon was found in other samples (seawater, surficial sediments, biota) collected during that week.

Our repeated failure to detect hydrocarbon concentration gradients in the water column indicates that these compounds are rapidly diluted and dispersed after discharge.

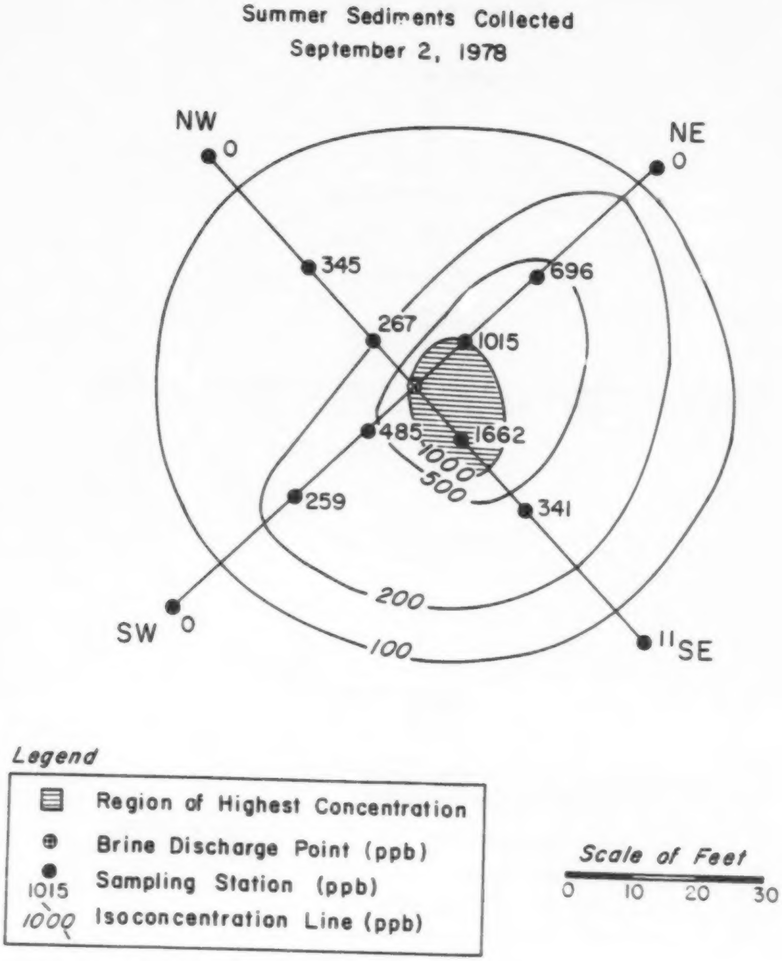
Summer Sediments Collected
September 2, 1978
NW
0
NE
0
345
696
267
1015
485
1662
1000
500
259
341
200
100
SW
0
11
SE
Legend
Region of Highest Concentration
Brine Discharge Point (ppb)
1015
Sampling Station (ppb)
1000
Isoconcentration Line (ppb)
Scale of Feet
0
10
20
30

Figure 10. Distribution of alkanes in surficial sediments on September 2, 1978.

6.5. SURFICIAL SEDIMENTS

Our initial studies (1976-77) were on samples collected from locations throughout the study area. When these failed to yield evidence of petroleum contamination, we focused our attention on the immediate vicinity of the production platforms.

6.5.1. Area-wide Studies

During 1976-77, alkane analyses were performed on samples from 45 locations selected for determination of trace metal content and measurement of sediment texture (Anderson *et al*., 1977). Only a few of these samples contained any evidence at all for petroleum hydrocarbons, and those samples were collected several kilometers from the production platforms.

6.5.2. Platform Studies

In general, we have found concentration gradients for alkanes in surficial sediments in the immediate vicinity of the production platforms; concentrations decreasing with increasing distance from the discharge. Anomalously low concentrations are sometimes found in sediments from below the structures, presumbly due to the scouring effects of currents round the legs of the structures.

On one occasion when sampling could not be completed in a single day and it extended into a second day, data were obtained which were consistent with prior observations of sediment resuspension in the region (Anderson *et. al*., 1977, 1979). On September 1, 1978 (Figure 9), samples were collected on transects running N, S, E, and W of the production platform. On the following day (Figure 10), samples were collected along intermediate transects. Significantly lower alkane concentrations were found on the second day, indicating that sediment resuspension had taken place.

A particularly notable feature of the hydrocarbons in the surficial sediments from below the production platforms is that they represent relatively fresh oil: i.e., the lighter alkanes were still present in these samples (Figure 11). Weathering would have eliminated these components. The n-heptadecane/pristane and n-octadecane/phytane ratios in the surficial sediments are similar to those in the produced water discharge.

6.5.3. Sulfur

Elemental sulfur was found in surficial sediments from locations close to the production platforms, but concentration gradients were not as pronounced as they were for the alkanes. Sulfur was also present in most of the other sediment samples collected elsewhere in the region.

The mean sulfur/alkane ratio was 17.4, considerably lower than in the produced water discharge. The maximum sulfur/alkane ratio observed was only 83.0. As in the case of the produced water discharge, there was no clear correlation between alkane and sulfur content.

Since there are no discharges from the well jackets, samples were taken from one such structure to determine whether there is any seepage of oil along the well pipes which might result in an additional input of petroleum hydrocarbons into the environment. Sulfur levels were also determined for these samples. There was no alkane concentration gradient in the vicinity of the well jacket. The mean alkane concentration for these samples was 0.12 ppm, less than 10% of the mean concentration (1.39 ppm) for the samples collected

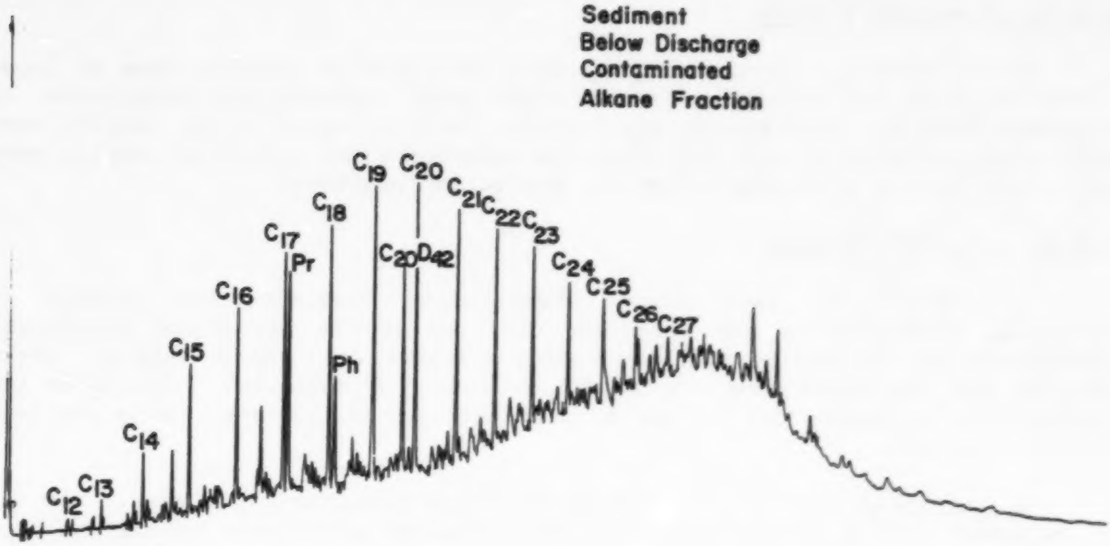

Figure 11. Gas chromatogram of alkane fraction of surficial sediment sample collected December 18, 1978 (sample LII).

from the general vicinity of the production platform, and considerably less than that of the samples collected below the production platform. Surprisingly, the sulfur concentrations near the well jacket (mean 4.10 ppm) are comparable to those near the production platform (mean 3.32 ppm). It seem likely that elemental sulfur is distributed throughout the region of the Buccaneer Field, but we have data only for samples collected in the vicinity of structures.

6.6. SEDIMENT TRAPS

These devices were designed and constructed by Anderson et al. (1979) for sampling particulate matter descending through the water column. They collected fish fecal pellets, bones, and scales, barnacles molts, tissue, and shell debris, bryozoans, algae, metal flakes, and fine sediments.

Petroleum hydrocarbons were usually not found in the contents of these traps. A typical analysis is represented in Figure 12, which provides evidence for the existence of an unusual C_{25} diolefin. We were unable to elucidate the precise structure of this compound, and cannot comment on its significance.

The sediment trap studies provided little evidence for the mode of transport of hydrocarbons through the water column.

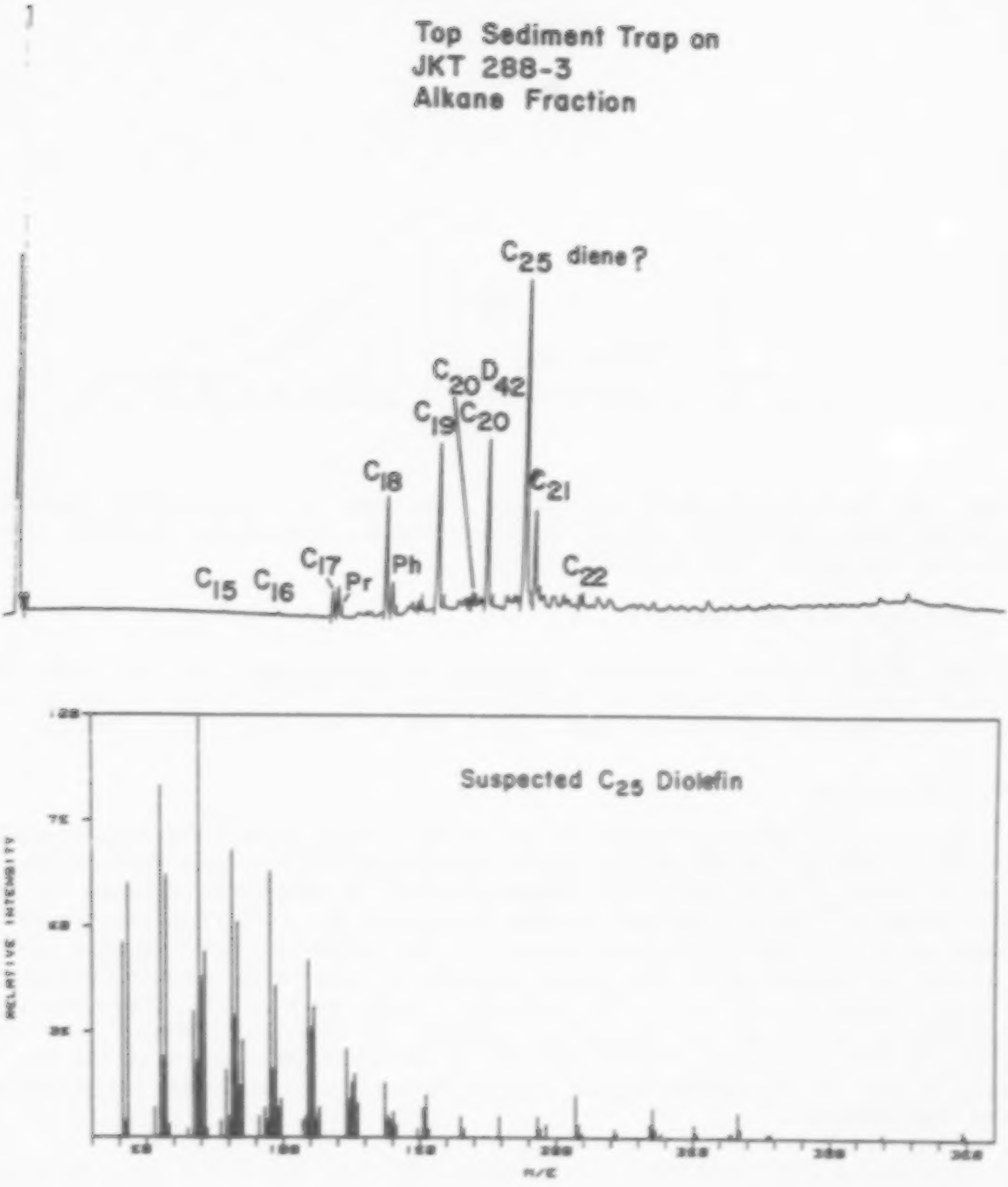

Figure 12. Gas chromatogram of alkane fracton of sediment trap sample (upper) and mass spectrum of an unusual C_{25} diolefin which it contained (lower). Sample collected November 28, 1978.

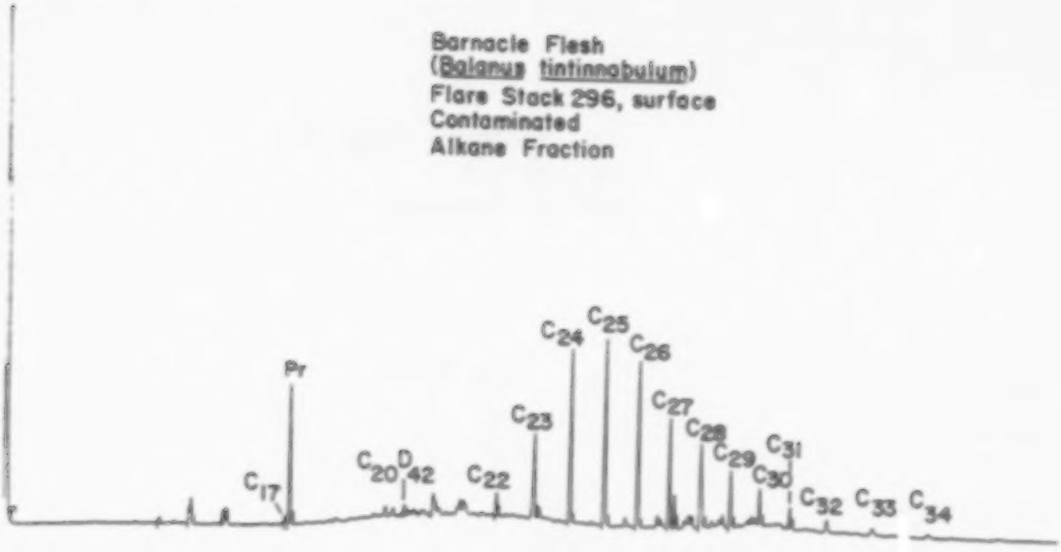

Figure 13. Gas chromatogram of alkane fraction of contaminated barnacles collected from the flare stack associated with Production Platform 296-A, collected August 26, 1978 (Sample VI).

6.7. PLATFORM FOULING COMMUNITY

The Mediterranean barnacle (*Balanus tintinnabulum*) is the most conspicuous member of the platform fouling community. This population has been fully characterized by Fotheringham (1977) and by Gallaway (1979, 1980).

6.7.1. Barnacles

During the first two years of the study, flesh from barnacles collected from the production platforms at depths approximately 3 m from the surface was found to contain relatively high concentrations of petroleum alkanes (up to 4 ppm). Those collected from the air/sea interface and at depths greater than 3 m were generally devoid of contaminants. Oil tends to float at the air/sea interface so barnacles in the upper portion of the water column receive the greatest exposure to it. We suspected that more rapid degradation of hydrocarbons occurred in barnacles exposed to the air and/or sun, thus explaining the low alkane concentrations in barnacles collected at the air/sea interface and the somewhat higher concentrations in specimens collected 3 m below the surface.

Degradation of petroleum hydrocarbons in the barnacles was apparently efficient. Figure 13 contains data for a barnacle containing 16 ppm of these compounds; it contains lower relative concentrations of the lighter alkanes than are observed in surficial sediments.

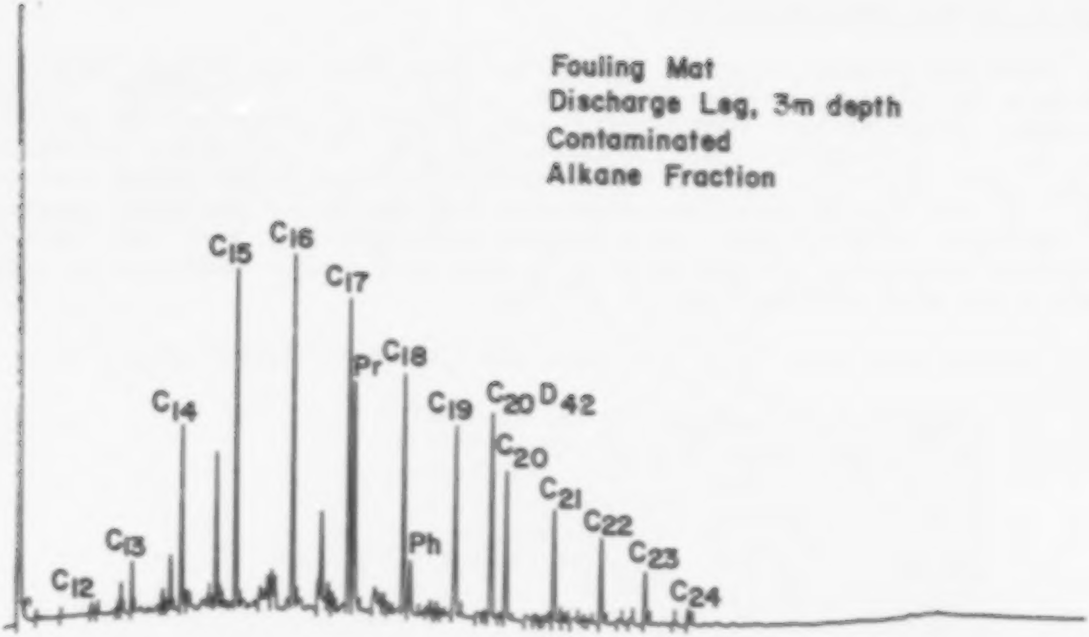

Figure 14. Gas chromatogram of alkane fraction of contaminated fouling mat collected August 26, 1978 (sample number I).

Curiously, almost all of the barnacles collected during the final two years of the study contained very low concentrations of petroleum hydrocarbons. We used similar analytical procedures for barnacles throughout the study, so there is probably no systematic error that could account for this observation, and we have no alternative explanation for the higher concentrations found during the first two years.

6.7.2. Fouling Mat

Some analyses were performed on barnacle shells and their attached organisms, while other analyses were performed on aggregations of the fouling mat. Similar results were obtained from each type of sample. Most samples contained petroleum hydrocarbons, and concentrations were particularly high in those collected just below the air/sea interface. A typical chromatogram for the fouling mat is given in Figure 14.

6.8. FISH

A large number of fish, representing more than 30 species, was collected for hydrocarbon analysis during the first two years of the project. During subsequent years, when we had more information on the feeding habits and habitats of the different species, we concentrated on four species which we considered to be particularly significant on the basis of their positions in the food web.

6.8.1. Initial Studies (1976-78)

When the project commenced, little was known about the feeding habits or habitats of the fish which could be captured in the Buccaneer Field. Moreover, there was some controversy in the literature concerning the ability (or not) of any marine organisms (including fish) to incorporate petroleum hydrocarbons into their tissues and to concentrate them as they passed through the food web. Consequently, we obtained a wide variety of individual species to determine their content of petroleum hydrocarbons. With the limited resources available, we were able to examine only single specimens of some species and only a few specimens of others.

Species which were found to contain petroleum hydrocarbons were:

Archosargus probatocephalus (sheepshead)
Centropristis philadelphica (rock sea bass)
Chaetodipterus faber (Atlantic spadefish)
Cynoscion arenarius (sand seatrout)
Lutjanus campechanus (red snapper)
Micropogon undulatus (Atlantic croaker)
Pomatomus saltatrix (bluefish)
Porichthys porosissimus (Atlantic midshipman)
Prionotus rubio (blackfin searobin)
Saurida brasiliensis (largescale lizardfish)
Stenotomus caprinus (longspine porgy)
Syacium papillosum (dusky flounder)
Symphurus plagiusa (blackcheek tonguefish)
Synodus foetens (inshore lizardfish)
Urophycis floridanus (southern hake)

Species for which it was not possible to decide whether petroleum hydrocarbons were present or absent were:

Arius felis (sea catfish)
Ogcocephalus parvus (roughback batfish)
Opsanus pardus (leopard toadfish)

Species which were not contaminated were:

Balistes capriscus (gray triggerfish)
Citharichthys spilopterus (bay whiff)
Diplectrum bivittatum (dwarf sand perch)
Echeneis naucrates (sharksucker)
Haemulon aurolineatum (tomtate)
Kyphosus incisor (yellow chum)
Lagodon rhomboides (pinfish)
Menticirrhus americanus (southern kingfish)
Orthopristis chrysoptera (pigfish)
Peprilus burti (Gulf butterfish)
Prionotus ophryus (bandtail searobin)
Scorpaena calcarata (smoothhead scorpionfish)
Serranus subligarus (belted sand bass)

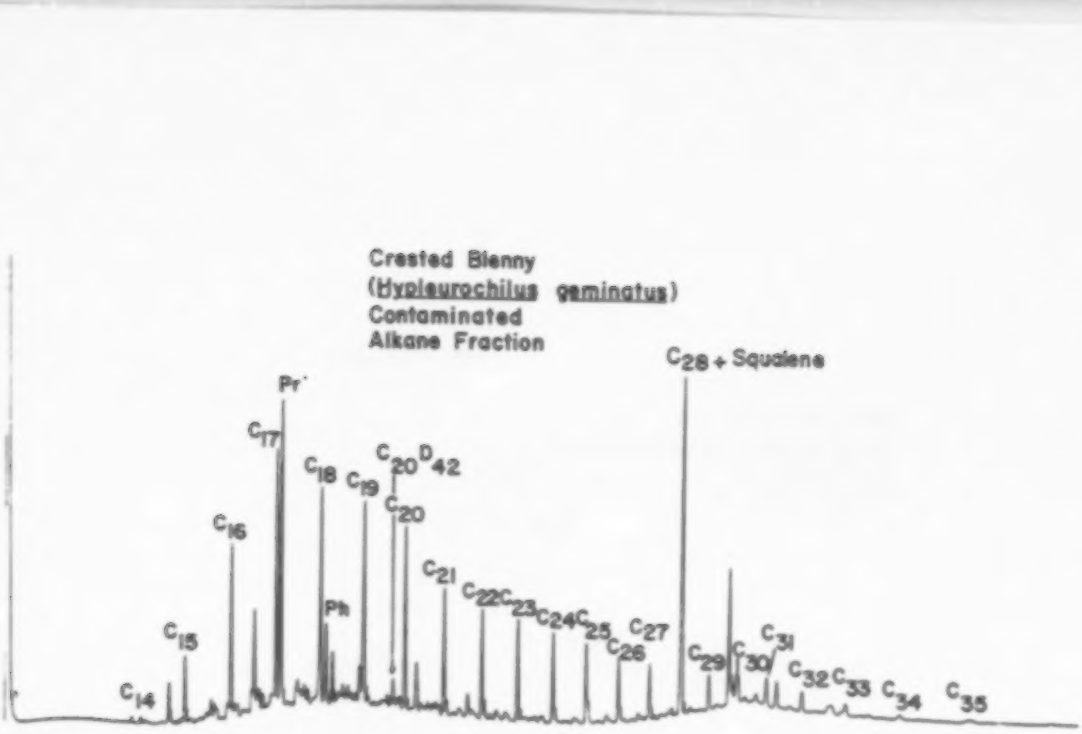

Figure 15. Gas chromatogram of alkane fraction of crested blenny collected March 26, 1979 (sample CB20).

All that we could conclude was that half of the fish that we examined were contaminated, and half were not. The numbers of specimens of each species were too small for us to decide whether any particular species was more succeptible than others to petroleum contamination.

6.8.2. Crested Blenny (Hypleurochilus geminatus)

Blennies are small fish which feed on and among the platform fouling community. They were also found to be habitat faithful (Gallaway, 1979). Since portions of the fouling community are contaminated with petroleum hydrocarbons (see above), it was of interest to determine whether the blennies became contaminated also.

Virtually every specimen of crested blenny examined contained petroleum alkanes. Concentration maxima were usually in the range C_{20} to C_{31}. A typical analysis is shown in Figure 15. In this specimen, the n-octadecane/phytane ratio is similar to that of the produced water, but the n-heptadecane/pristane ratio is distorted by the presence of endogenous pristane of biogenic origin. The mean alkane concentration in this species was 6.8 ppm.

6.8.3. Sheepshead (Archosargus probatocephalus)

The sheepshead was also found to be habitat faithful. It is well equipped to crush barnacle shells, and consumes their flesh. It also consumes swimming crabs (Gallaway, 1979). Petroleum alkanes were found in about half of the muscle samples from this species and in about a quarter of the liver samples. Typical chromatograms for contaminated muscle and liver samples are given in Figure 16. Concentration maxima were generally at C_{25} or C_{26} for

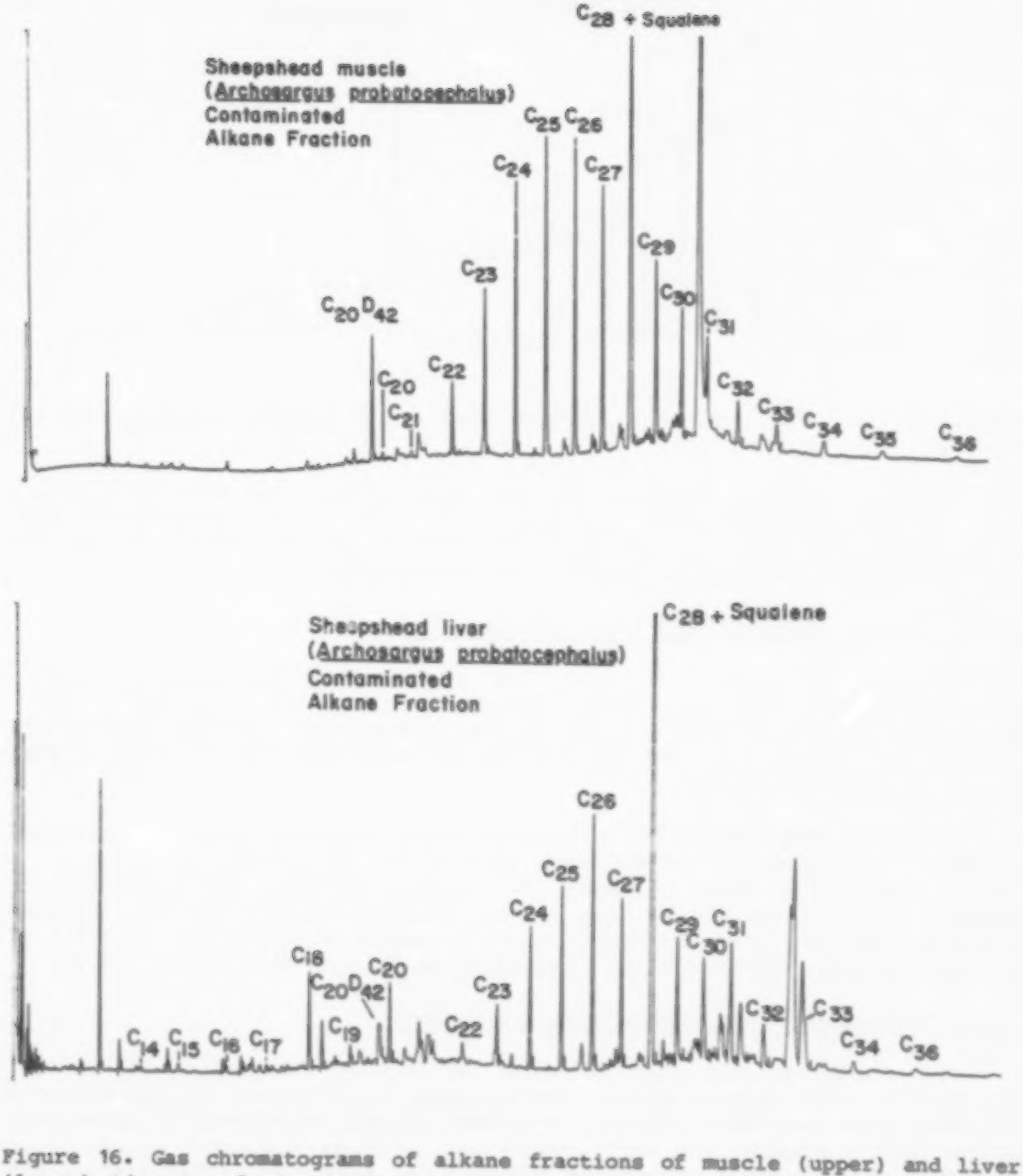

Figure 16. Gas chromatograms of alkane fractions of muscle (upper) and liver (lower) tissues of sheepshead collected August 24, 1978 (liver: sample II; muscle: sample XXX).

both tissue types. The mean alkane concentrations in muscle and liver tissue were 4.6 and 6.1 ppm, respectively.

6.8.4. Spadefish (*Chaetodipterus faber*)

The spadefish is another species which is habitat faithful, but it feeds mainly in the water column (Gallaway, 1979) so one would not expect it to be exposed to petroleum hydrocarbons to the same degree as the crested blenny or sheepshead which feed on the more contaminated sessile organisms. Indeed, the mean alkane concentrations in muscle and liver samples were, respectively, 0.6 and 2.0 ppm.

6.8.5. Red Snapper (*Lutjanus campechanus*)

Red snapper apparently migrate to the structures in the Buccaneer Field from a wide region, and become habitat faithful after they arrive. They feed on smaller fish and other organisms (Gallaway *et al.*, 1979). One might expect these fish to be less contaminated than other species: they were included in the detailed study because they are prized by sports fishermen. About a quarter of the specimens examined contained petroleum alkanes in both their livers and in muscle tissues. The mean concentrations were 1.1 and 1.3 ppm, respectively. The range of hydrocarbon concentrations for this species was much greater than for the crested blenny, sheepshead, and spadefish. This might reflect the fact that some specimens had been resident in the region of the Buccaneer Field longer than others.

6.9. SHRIMP

Four species of shrimp were examined: *Penaeus aztecus* (brown shrimp), *Penaeus duorarum* (pink shrimp), *Squilla empusa* (mantis shrimp), and *Trachypenaeus similis* (sugar shrimp). Figure 17 shows data for an uncontaminated brown shrimp and one which contains 2.5 ppm of petroleum alkanes. The latter specimen was the only shrimp encountered which contained any significant quantity of petroleum hydrocarbons, most contained none at all. Shrimp are highly migratory so individual animals would not be expected to spend much time in the region of the Buccaneer Field. This would reduce their probability of ingesting Buccaneer Field contaminants.

6.10. OTHER BIOTA

Squid and plankton samples collected in the course of other components of the study were examined for their content of petroleum hydrocarbons. In addition, some sessile benthic organisms were collected specifically for us to determine whether they accumulated petroleum hydrocarbons.

6.10.1. Squid

We examined white squid (*Lolliguncula brevis*) collected on four occasions during the first year of the study. None contained petroleum hydrocarbons.

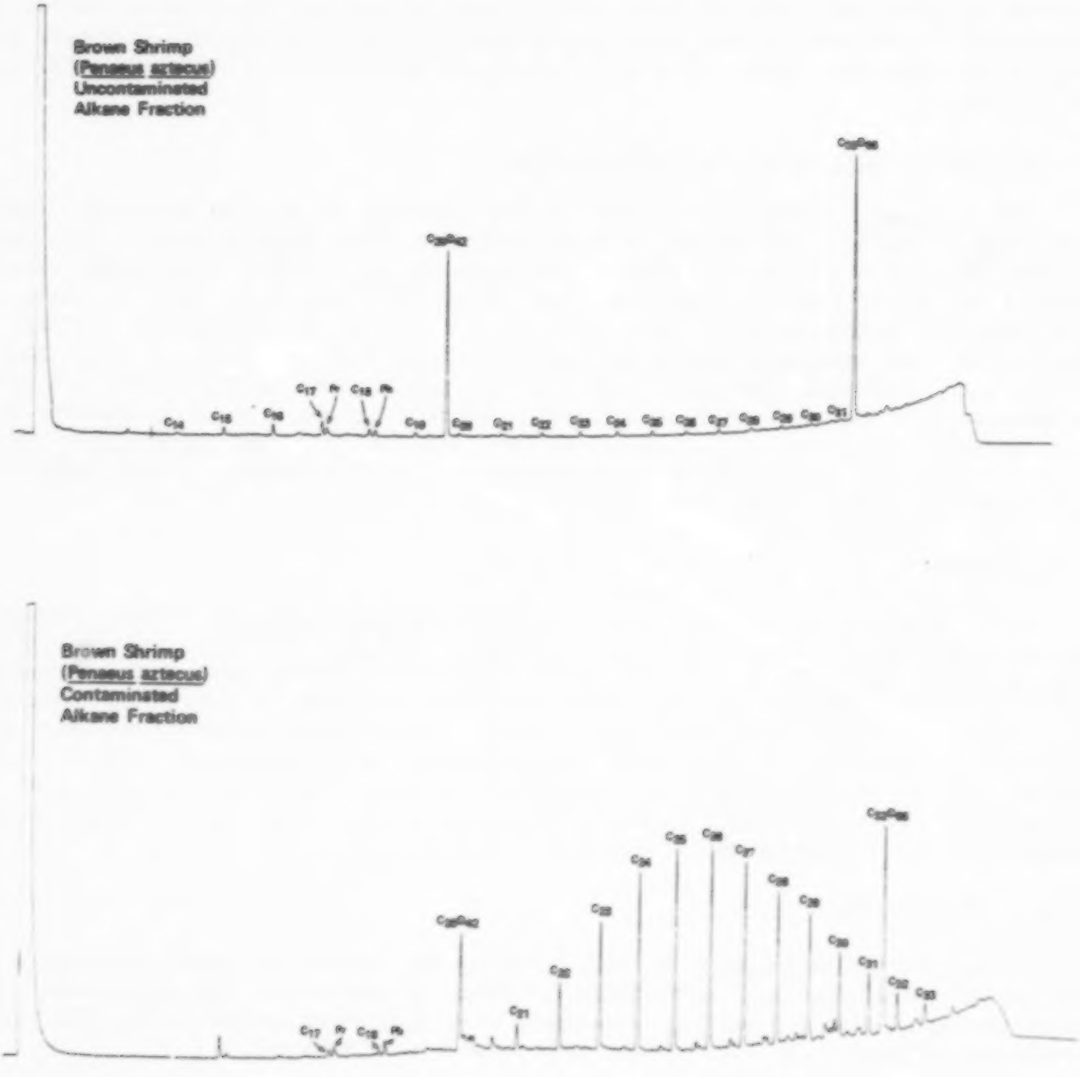

Figure 17. Gas chromatograms of alkane fractions of uncontaminated (upper: sample I, August 9, 1976) and contaminated (lower: sample III, August 10, 1976) brown shrimp.

6.10.2. Plankton

Plankton samples were collected both at the air/sea interface and from the water column. No attempt was made to separate and analyze the individual species; a copepod (*Acartia tonsa*), the sergestid shrimp (*Lucifer faxoni*), and a chaetognath (*Sagitta tenuis*) were among the major species obtained (Fotheringham, 1976; Fotheringham and Brunenmeister, 1975).

The majority of surface plankton samples were contaminated with petroleum alkanes. In two samples, tar balls were readily visible; these have been reported present during microscopic examination of other samples from the same location (Finucane, 1979). The majority of subsurface samples contained only biogenic hydrocarbons: n-C_{15}, n-C_{17}, and pristane. It is possible that the petroleum hydrocarbons observed in surface samples were not contained within the plankton (inside the organisms), but were due to the presence of minute particles of tar. This is still important since biota feeding on plankton would just as likely ingest tar balls as plankton.

6.10.3. Benthic Organisms

Like barnacles, many benthic organisms are sedentary. Examination of species representative of the ecology of the study area provided a more complete picture of the effects of oil production. Forty-eight samples from the classes Bivalvia, Gastropoda, Hydrozoa, and Anthozoa collected from the production platforms, quarters platforms, and well jackets were analyzed. Species examined were:

Alcyonaria (yellow coral)
Arbacia unctulata (sea urchin)
Chloeia viridus (brittle worm)
Fasciolaria hunteria (banded tulip shell)
Hydroida (brown hydroid)
Murex fulvescens (giant eastern murex)
Pagurus floridanus (hermit crab)
Pleuroploea gigantea (Florida horse conch)
Pteria colymbus (winged oyster)

All but one of the Alcyonaria samples contained alkanes in the C_{22} to C_{32} region. While this has been used as an indicator for pollution in other samples, there is evidence that these compounds are biogenic (Koons *et al.*, 1965). Representatives from the class Hydroida had similar profiles, but only one sample from the well jacket location was analyzed so it was not possible to determine whether the hydrocarbons in the production platform samples were the result of oil production activities. Few of the specimens of *Pteria colymbus* collected at the production platform contained petroleum alkanes, while they did contain methylnaphthalenes and benzo[*a*]pyrene. Other species of molluscs (*Mytilus edulis*) have been postulated to metabolize aliphatic and olefinic hydrocarbons but not aromatics (Ehrhardt and Heinemann, 1975). This could also be possible for *P. colymbus*. Specimens of a more mobile mollusc, *Pleuroploea gigantea*, had various hydrocarbon profiles which could be ascribed to petroleum contamination. The number of specimens of other species was not large enough to allow for any valid conclusions.

6.11. LIPIDS

Our interest in lipids dates from the first year of the study. At that time, we had little information concerning the nature of the food web in the Buccaneer Field and we had hoped to trace some of the pathways by identifying the sterols in key organisms. This approach became redundant after direct observations concerning habitats and feeding habits were initiated by Gallaway *et al*. (1979, 1980).

We renewed our interest in lipids during the fourth year of the study after we had found (during a separate study) evidence for a relationship between dietary lipids and ovarian maturation and spawning in penaeid shrimp.

6.11.1. Sterols in the Food Web

Sterols of invertebrates from the region of the Buccaneer Field were examined both as the free sterols and their TMS ethers using packed GC columns, and GC-MS was used for the final identification (Brooks and Middleditch 1973).

The structures in the Buccaneer Field support a relatively isolated reef ecosystem. If the sterols are unchanged in their composition as they pass through the food web, the steroid profiles of the various organisms would be expected to be similar to those of the plankton. This is generally the case (Table 5). A major exception is the squid, which is capable of biosynthesizing sterols: the endogenous cholesterol predominates over dietary sterols in these specimens. Also, as anticipated (Fagerlund and Idler 1957), the barnacles contain relatively high concentrations of desmosterol. The sea urchins and polychaete worms, while capable of synthesizing sterols, also contain sterols which are of presumed dietary origin. The shrimp are incapable of the synthesis of sterols *de novo*, although they can accomplish the interconversion of certain sterols. This is apparently what is happening here. These specimens do not reflect the diversity of sterols found at the base of the food web (shrimp are able to convert C_{28} and C_{29} sterols to cholesterol), but the minor sterols are undoubtedly of dietary origin. In these analyses, whole shrimp were examined. However, in other analyses of *P. setiferus* from the Gulf of Mexico and mariculture facilities, we have examined individual tissues. We find that there is a great diversity of sterols in the hepatopancreas, presumably reflecting the dietary composition, and less diversity in the gonads, while the tail muscle contains mainly cholesterol and 22-dehydrocholesterol (Middleditch *et al*., 1980b).

6.11.2. Maturation and Spawning of Penaeid Shrimp

We have found in the laboratory (Brown *et al*., 1979, 1980; Lawrence *et al*., 1980; Middleditch *et al*., 1979, 1980a) that certain lipids are required for ovarian maturation of penaeid shrimp, and that they are incorporated into eggs that are viable (Ward *et al*., 1979). In our preliminary studies, we used bloodworms (which are rich in the required lipids) to induce maturation. We have also found that the lipid composition in individual components of a food web is fairly homogeneous. Thus, the sterol profiles of plankton, barnacles,

TABLE 5. MAJOR STEROLS IN MARINE INVERTEBRATES COLLECTED FROM THE REGION OF THE BUCCANEER FIELD DURING SUMMER, 1976.

Specimen	A[a]	B	C	D	E	F
PLANKTON						
Mixed zooplankton	3.8[b]	13.8	62.4	14.3[c]	3.8[d]	1.9[e]
SQUID						
Loliguncula brevis		2.0	98.0			
SEA URCHIN						
Arbacia unctulata	2.4	6.5	80.6	10.5[c]		
POLYCHAETE WORM						
Choloeia viridis	1.7	7.7	85.5	3.4[c]	1.7[f]	
BARNACLE						
Balanus tintinnabulum	1.2	11.6	60.8	24.9	1.5	
SHRIMP						
Penaeus aztecus		2.0	98.0			
Penaeus duorarum	1.0	1.9	95.2	1.9		
Trachypenaeus similis		2.0	98.0			
Squilla empusa	1.0	2.9	96.1			

[a] A = 22-*trans*-24-norcholesta-5,22-dien-3β-ol, B = 22-dehydrocholesterol, C = cholesterol, D = desmosterol, E = 24-methylcholesta-5,22-dien-3β-ol, F = sitosterol, [b] also contains 22-*trans*-24-norcholest-22-en-3β-ol, [c] also contains 24-methylcholesterol, [d] also contains 24-methylcholestadienol, [e] also contains 24-ethylidenecholesterol, [f] also contains 22-dihydroergosterol.

squid, polychaetes, sea urchins and four species of shrimp from the region of the Buccaneer Field have many features in common (Chang, 1978). Also, the fatty acid profiles of a wide range of invertebrates from West Bay, Galveston are very similar (Middleditch *et al.*, 1980b). We can conclude that the species consumed by the shrimp are less important to maturation than the lipids present in the food web. The primary producers of many of these lipids are the benthic algae, so one would expect to be able to determine whether a particular site is conducive to spawning by examining lipid profiles of the sediments (where the shrimp normally feed). Indeed, our analyses of sediments from shrimp spawning sites located during a study of the Bryan Mound Strategic Petroleum Reserve brine disposal site off Freeport, Texas have revealed the presence of the lipids suspected of being important for ovarian maturation and spawning of penaeid shrimp.

Dietary carotenoids are also needed for ovarian development and the production of viable eggs (Zagalsky et al., 1967). These compounds are also available from sediments (Schwendinger and Erdman, 1963). A colorimetric procedure was used for determining carotenoid concentrations, which are expressed in "β-carotene equivalents."

Sediments from the Buccaneer Field contained sterols, fatty acids, and carotenoids. The sterol fraction was dominated by cholesterol, and there were smaller amounts of 22-dehydrocholesterol and desmosterol. A wide range of fatty acids was encountered, including the polyunsaturated compounds suspected of being vital to ovarian maturation and spawning. No attempt was made to identify individual carotenoids.

Thus, all of the lipids suspected of being required to stimulate ovarian maturation and spawning are indeed present in the sediments. However, our current state of knowledge is devoid of information concerning the quantities of these lipids that are required in the diet, and concerning other parameters which may be important for ovarian maturation.

SECTION 7

DISCUSSION

The conventional method of assessing effluents from offshore production platforms has included measurements of "total oil" by spectrophotometric methods. Our early results showed that it was more appropriate to consider the effluents as a medium containing a number of individual substances; different relative concentrations of these substances could be present in effluent samples containing the same amount of "total oil." During earlier reviews of our research, we suggested that monitoring of individual toxic components of the effluents would be more appropriate than monitoring "total oil." The proposed new Ocean Discharge Criteria (Federal Register, February 12, 1980) include a provision for monitoring effluents for a specific list of toxic pollutants ("priority pollutants").

The intent of these proposed regulations is to protect the environment from exposure to harmful amounts of specific substances with known toxic properties. It appears that the main concern in drafting these regulations was related to limiting the concentrations of toxic substances in the mixing zone below the discharge pipe. The assumption appears to have been made that there is no other location in the region of an oil field which contains significant quantities of contaminants.

We have indeed found that the mixing zone is the only component of the water column in which measurable quantities of petroleum hydrocarbons and sulfur can be seen. Dispersion of these contaminants appears to be rapid and efficient. Observations by Gallaway (1980) indicate that there is only minimal damage to the platform fouling community which can be ascribed to the discharge. If the rate of discharge of produced water from the platforms were to be increased, we are tempted to suggest that little, if any, additional damage to the fouling community would result. If, however, the concentration of the contaminants in the discharge were to be increased beyond a critical level, the factors which control dispersion and dilution in the water column may be insufficient to protect the fouling community from significant damage. Under such circumstances, effects might also be transmitted to other components of the food web. We have insuffecent information to determine the critical concentration of contaminants at this time, so we are unable to recommend any specific increase in permitted concentrations of contaminants. This appears to be the philosophy of the proposed Ocean Discharge Criteria: limits are imposed upon the concentrations of components of the discharges based upon the state-of-the-art of analytical chemistry, rather than on an assessment of potential harm to the environment.

We feel that some consideration should be given also to the pool of contaminants discovered in the surficial sediments below the production platforms. We venture to suggest that the sediment concentrations of these contaminants depend upon the total quantities of contaminants discharged from the production platforms rather than the concentrations of contaminants in the discharges. Of course, other factors such as water depth, currents, rates of sediment resuspension and deposition, and mode of transport through the water column will also contribute to the concentration of contaminants in the surficial sediments. Therefore, to minimize the size of this pool of contaminants, both the rate of discharge of produced water and its content of toxic substances should be limited. Again, we have insufficient data to suggest critical values for these parameters. We should add that, in the Buccaneer Field, no adverse effects were found which could be ascribed to the presence of contaminants in the surficial sediments.

There are at present no mandated analytical procedures for the analysis of the organic toxic pollutants, although proposed methods based upon gas chromatography (GC), high-performance liquid chromatography (HPLC), and combined gas chromatography - mass spectrometry (GC-MS) have been described (Federal Register, December 3, 1979). It was indicated in the recently issued Consolidated Permit Regulations that GC-MS would be the method of choice in most instances (Federal Register, May 19, 1980). With the detection limits cited for the proposed GC-MS method, only five organic toxic pollutants would have been reported: acenaphthylene, benzene, ethylbenzene, naphthalene, and toluene. We have in fact found additional organic toxic pollutants at lower concentrations, and we have also found other toxic substances which are not on the formal list of organic toxic pollutants. The priority pollutants were chosen during a consideration of effluents from a wide range of different industries. Most of them will not be found in discharges from offshore production platforms. Conversely, there are toxic substances that we have identified in the effluents which are not on the list of priority pollutants. A more appropriate list of substances to be monitored could be prepared for this industry. This revised list could include alkylated homologs of the aromatic hydrocarbons, since they are similar in physical properties and toxicity to the parent compounds. We should also point out that, of the methods of analysis listed above, only GC-MS provides sufficient sensitivity and specificity for characterizing these complex effluents.

SECTION 8

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